ADSORPTION OF LEAD (II) FROM AQUEOUS SOLUTION BY ACTIVATED CARBON DEVELOPED FROM MANGROVE WOOD BY MICROWAVE RADIATION HEATING

by

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Sincerely,
Hajar binti Tan Lekha @ Malek

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LIST OF SYMBOLS

C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Highest initial adsorbate concentration	mg/L
K_F	Freundlich isotherm constant	mg/g $(L/mg)^{1/n}$
K_L	Rate of adsorption for Langmuir isotherm	L/mg
n_F	Constant for Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Adsorption capacity for Langmuir isotherm	mg/g
R^2	Linear regression correlation coefficient	-
R_L	Dimensionless constant separation factor	
t	Time	Minute or hour

LIST OF ABBREVIATIONS

AC	Activated carbon
CO_2	Carbon dioxide
N_2	Nitrogen gas
Pb	Lead
RSM	Response Surface Methodology

ABSTRAK

Kajian ini bertujuan untuk menghasilkan karbon teraktif yang berasal dari kayu bakau untuk menjerap ion logam berat iaitu ion plumbum (II). Bahan penjerap diaktifkan melalui pengaktifan fizikal dengan pemanasan gelombang mikro dan gasifikasi nitrogen (NO_2). Kajian mengenai kesan keadaan operasi terhadap pengaktifan bahan penjerap dilakukan dengan mendedahkan arang pada waktu radiasi dan daya radiasi yang berbeza. Pengoptimuman karbon aktif dilakukan dengan menggunakan metodologi permukaan tindak balas (RSM) Keadaan optimum yang diperoleh untuk karbon aktif yang disediakan adalah pada waktu radiasi 2 minit dan daya radiasi 528.66 watt. Penyingkiran ion plumbum (II) dalam sistem kendalian kelompok dilakukan dengan menyelidiki beberapa parameter seperti kepekatan awal ion plumbum (II), masa kontak, suhu larutan dan pH larutan. Dalam kajian ini, penyingkiran ion plumbum (II) tertinggi dalam sistem kendalian kelompok pada pH 4, kepekatan awal plumbum (II) pada 10 mg / L dan masa hubungan optimum pada 30 minit. Kajian garis sesuhu dilakukan dan hasilnya menunjukkan bahawa sistem penjerap-bahan penjerapan bersesuaian dengan baik pada model garis sesuhu Langmuir dibandingkan dengan model garis sesuhu Freundlich.

ABSTRACT

Activated carbon is an adsorbent that is large in surface area with a great amount of porous structure formed on it. Activated carbon is utilised as an adsorbent because of the effectiveness for adsorbing a wide type of contaminants in liquids or gases. This study aims to develop an activated carbon derived from the mangrove wood to adsorb heavy metal which is lead (II) ions. The adsorbent was activated via physical activation by microwave heating and gasification of nitrogen (NO_2). Study on the effects of the operating condition on the activation of the adsorbent was performed by exposing the char at different radiation time and radiation power. The optimization of the activated carbon was performed by using response surface methodology (RSM). The optimum condition obtained for the prepared activated carbon was at radiation time of 2 minutes and radiation power of 528.66 watt. Removal of lead (II) ions in batch system was performed by investigating several parameters such as initial lead (II) ions concentration, contact time, solution temperature and solution pH In this studies, the highest removal of lead (II) ions in a batch system was at pH 4, initial lead concentration of 10 mg/L and the optimum contact time of 30 minutes. The isotherm studies were performed and the results show that the adsorbate-adsorbent system fitted well to the Langmuir isotherm model compared to Freundlich isotherm model. In this study, the adsorption reaction performed by using activated carbon prepared from mangrove wood was found to be effective in removing high percentage of lead (II) ions.

CHAPTER 1 INTRODUCTION

Commonly, the source of the heavy metal pollution in the waterbodies happens near to the industrial area. This occurrence is due to the untreated effluent of the waste from the industries or inefficient treatment method employed by the industries. The result to this scenario can cause serious harmful effect to the living organism and the environment if they were exposed for longer time.

It has been reported that there are 55 rivers in Malaysia has exceeded the cadmium limit and 44 rivers has exceeded iron metal limit while 36 of the rivers has exceeded the lead limit (Shahbudin & Kamal, 2020). The remaining rivers have high mercury concentration (Shahbudin & Kamal, 2020). These contaminants weredischarged in the wastewater which were not treated properly by the factories nearby to the water bodies. The increment of the contaminants is due to the increase in the number of industrial activities mainly in urban area which eventually lead to improper management of the heavy metals discharge. This situation can cause various health issues as well as results to serious environmental impact.

Thus, mitigation steps need to be considered to reduce the harmful impact caused due to the ineffective treatment of wastewater employed by the industries. There are several treatments that can be opted by the industries to ensure the standard limit of heavy metal is complied. Although there are various methods of treatment available nowadays, the effectiveness of the process is not really promising and may not be environmentally friendly.

1.1 Research Background

With the increasing of world's population, the usage of heavy metal increase in various industrial activities such as electroplating, mining, battery production, tanning and galvanizing. Heavy metals are a group of metals and metalloids that have high densities and toxic even at part per billion (ppb) levels. The most common toxic heavy metals in industrial wastewater are arsenic, lead, mercury, cadmium, chromium, copper, nickel, silver and zinc.

The waste generated from industries are the major contribution of environmental pollution. The effluents generated from the manufacturers such as electroplating industries, mining field, electronic tools and production of battery consist of high percentage of heavy metals which are toxic to the marine life as it disturbs the biological activities in the water system (Kadirvelu et al., 2003; Rozaini et al., 2010). Sewage which is also a part of the wastewater that contains faeces or urine. Sewage which comes from domestic, municipal or industrial wastewater may also be contaminated with pathogens, heavy metal and many toxic chemicals.

It has been reported that the heavy metal in the sewage sludge contains approximately 80-90% of heavy metal which will affect the treatment of the wastewater (Tytła, 2019). Commonly, the heavy metal traced in the industrial wastewater are copper, lead, zinc, cadmium, chromium, iron and manganese. There are several conventional approaches investigated by the authorities such as chemical precipitation, chemical coagulation and chemical oxidation to reduce the concentration of dyes and metal ions in the wastewater so that it meets the standard requirement enforced (Kadirvelu et al., 2003).

1.1.1 Lead ion in wastewater

Method on removal of heavy metal ions from sewage mainly in mining waste effluents has been extensively studied in many years. Lead which bluish grey in colour, soft and malleable are known to be very toxic to the environment. It is found in the soil, air and water.

It has been reported that the exposure of this heavy metal can cause serious health problems which are anaemia, kidney failure and damage to brain's tissue (Acharya et al. 2013). Industries such as battery manufacturing and metal plating mostly will contain lead in their water discharge which mainly cause the pollution in the waterbodies. The average lead concentration in the waste generated from the industries is approximately 200 – 500 mg/L (Arbabi et al., 2015). The concentration of lead generated from the industry is higher as compared to the acceptable discharge concentration of wastewater from industries set by the authority. Thus, effective treatment must be implemented by the industries before discharging the wastewater to the waterbodies. Few reliable methods that have been widely studied for removal of lead from the wastewater are chemical precipitation, ion exchange, electro-coagulant, membrane filtration and adsorption.

1.1.1(a) Chemical precipitation

Chemical precipitation is a commonly implemented method where it is used to remove lead from the wastewater streams. It is a simple and economical technique for reducing high concentration of lead in the wastewater. It works by adding a correct amount of anion into the wastewater, thus, resulted to the formation of lead ion precipitate. However, the efficiency of the precipitation process is affected by the pH of the solution and the presence of other salts (ions) (Ahluwalia & Goyal, 2007). At low concentration, removal of lead using chemical such as lime, bisulphide or ion exchange is ineffective (Ahluwalia & Goyal, 2007).

1.1.1(b) Ion exchange

Ion exchange method is an expensive as compared to other methods. Through this technique, large volume of waste can be handled to achieve low concentration of heavy metal ions (Arbabi et al., 2015). Ion exchanger is a solid that able to exchange either cations or inions from the electrolyte solution. The matrices used for ion exchange commonly is synthetic organic ion exchange resins (Ahluwalia & Goyal, 2007). However, this method has a few disadvantages in handling high concentration of lead ions as the matrix will easily fouled by organics and other impurities contained in the wastewater. In addition, ion exchange treatment gets easily sensitive to the pH of the solution (Ahluwalia & Goyal, 2007).

1.1.1(c) Electro-coagulant

Electrochemical reaction involves the transfer of ion, atom or molecule aided by the electric current supplied to the ionic solution and electrode. Electro-coagulant is same as electrochemical where current is used to eliminate the lead ions from the solution. Electrical charge is introduced to the wastewater. The positive lead ion will be neutralized with the opposite charge supplied to the wastewater and forming precipitation due to the destabilization reaction occurred.

1.1.1(d) Membrane filtration

Membrane filtration is one of the alternatives for removal of lead ion. This method depends on the size of the ion that will be retained. There are few techniques under the membrane filtration which are ultrafiltration, nanofiltration and reverse osmosis.

1.1.1(e) Adsorption

Adsorption is the process where ions or molecules adhere to the surface of the adsorbent. In this method, activated carbon is found to be effective due to high capability to adsorb high amount of ions or molecules as the internal surface area is high. The effectiveness of the adsorption process depends on several aspects such as concentration of adsorbate, temperature of the solution and the polarity of the substances.

1.1.2 Activated carbon

Amidst the new technologies, an adsorbent which is known as activated carbon prepared by using an agricultural raw materials for the heavy metals removal has become a well-known method (Kadirvelu et al., 2003). The agricultural waste used can be coir pith (Santhy & Selvapathy, 2004), grape bagasse (Demiral & Güngör, 2016) orange peel (Moreno-Piraján & Giraldo, 2012), banana pith, maize cob, sago waste and coconut tree saw dust (Kadirvelu et al., 2003). Commonly, the material used to prepare an activated carbon is an organic material that is rich in carbon (Daud et al., 2017). This factor makes an activated carbon to be favourably used as an adsorbents due to the pore structure, high surface area, electron-conducting amphoteric tendencies and excellent adsorptive capacity (Ukanwa et al., 2019). These parameters are important in ensuring the effectiveness of the adsorption process as at high surface area and high porosity, the adsorption capacity will increase. The porosity and the surface area can be further increased by employing few activation methods such as physical, chemical and physiochemical activation. In term of chemical activation, different type of raw materials required different chemical agent and only favourable for certain metal ions table 1.1 shows the various type of chemical activation used for different raw materials for removal of metal ions.

Another factors that are considered to be important for the effectiveness of the adsorbent is the functional groups consists in the activated carbon. Activated carbon has few functional group which are carboxyl, carbonyl, phenol, lactone and quinone which are important for the adsorption reaction of the heavy metal ions (Heidarinejad et al., 2020). Other components such as oxygen, hydrogen, sulphur and nitrogen are also existed in the presence of functional groups or atoms of chemical in the structure of the adsorbent. Different functional groups are varied in each activated carbon, obtained from the activation processes, types of precursors and the thermal purification.

Table 1.1 Summary of application and chemical activation of the activation carbon

Raw materials	Method	Application	References
Grape bagasse	Phosphoric acid activation	Copper (II) ions removal	(Demiral & Güngör, 2016)
Orange peel	Potassium hydroxide activation	Chromium (II) ions, Cadmium (II) ions, Cobalt (II) ions	(Moreno-Piraján & Giraldo, 2012)
Coir Pith	Potassium hydroxide activation	Cadmium (II) ions, Copper (II) ions, Zinc (II) ions	(Santhy & Selvapathy, 2004)
Coconut tree sawdust	Sulfuric acid activation	Mercury (II), Nickel (II)	(Kadirvelu et al., 2003)
Sago waste	Sulfuric acid activation	Mercury (II), Nickel (II)	(Kadirvelu et al., 2003)
Maize cob	Sulfuric acid activation	Mercury (II), Nickel (II)	(Kadirvelu et al., 2003)
Banana pith	Sulfuric acid activation	Mercury (II), Nickel (II)	(Kadirvelu et al., 2003)
Mangrove barks	Sodium hydroxide activation	Copper (II) ions, lead (II) ions	(Oo et al., 2009)
Maize Tassel	Sulfuric acid activation	lead (II) ions	(Moyo et al., 2013)

1.2 Problem statement

Heavy metal pollution has become a major problem in aquatic system for many years (Hossen et al., 2015). Due to the high concentration of heavy metal wastewater effluent generated from the chemical-intensive industries, a proper treatment is implemented to reduce the harmful effect to the flora and fauna. According to the Environmental Protection Agency (EPA) of USA, the safe amount of concentration for lead to be discharged to the sewage system is 0.05-0.1 mg/L (Arbabi et al., 2015). However, the lead content in the industrial wastewater is approximately 200-500 mg/L (Arbabi et al., 2015). Studies have been performed widely for removal of lead in the wastewater by implementing few treatments such as adsorption, chemical precipitation, membrane filtration and electro-coagulation. However, some of the treatment have few limitations such as for precipitation process, the removal of lead (II) ions are ineffective at low concentration and insufficient to reduce the concentration of lead which fail to meet the specification of the water quality standard. In addition, ion exchange treatment method is nonselective and too sensitive to pH of solution. Thus, adsorption method is chosen as it is more economical and effective. Adsorption using activated carbon is known to be effective due to the high sorption capacity. The microporous nature of activated carbons is well suited for many applications such as molecular sieving and sorption. Therefore, the removal of lead (II) ions using optimized activated carbon will become more effective and promising.

The raw material chose in this study was mangrove wood. Research on the effect of preparation on optimized activated carbon using mangrove wood is yet limited. Thus, further study was performed to understand the effect of the preparation of the activated carbon on the yield and the surface characterization of this optimized adsorbent which later might affect the adsorption process.

1.3 Objective

The activated carbon was prepared at an optimum condition and studies on the effectiveness of the optimized activated carbon are performed by considering the objectives as below:

1. To prepare and optimize the activated carbon derived from mangrove wood.
2. To characterize the activated carbon prepared in term of surface morphology and elemental.

3. To investigate the effect of different variables such as pH, contact time, initial lead (II) ions concentration and initial adsorbent dosage on the adsorption capacity of lead (II) ions on the adsorbent.
4. To analyse the isotherms of the activated carbon prepared from mangrove wood.

1.4 Report Contents

In this study, mangrove wood was used as a precursor of activated carbon. The adsorbent was activated by using microwave radiation method where the preparation condition for the adsorbent was variated at different radiation power and time. The radiation power was set at different reading which were 364, 490 and 616 watt while the radiation time were at 2, 4, 6 minutes. Batch adsorption study was performed to determine the highest removal of lead (II) ions. The optimization procedure was conducted by using Design Expert 6.0.6 (STAT-EASE Inc., Minneapolis USA) software.

Equilibrium study on the adsorbent was then performed by variating the parameters such as contact time, initial concentration of adsorbate, pH and temperature of solution. The optimum condition for the adsorption process was determined at the highest percentage of removal of lead (II) ions and adsorption capacity.

The morphology and elemental study on the activated carbon was conducted by using SEM and CHNS respectively.

Study on the adsorption isotherm was conducted by employing Langmuir and Freundlich isotherm. The result was plotted and the correlation value, R^2 was being compared to determine the most well fitted isotherm model.

CHAPTER 2 LITERATURE REVIEW

2.1 Description of heavy metals

Heavy metals can adversely affect the public health due to their toxicity and its characteristic which is a non-biodegradable in nature. High concentration and long exposure of heavy metals contaminants to the human beings and animals can lead to a serious health condition. Different type of heavy metals exposure will result to different condition of health issues. Table 2.1 summarise the health effect caused by the heavy metal. Human may be exposed to the heavy metal through various ways such as ingestion through food and drink, inhalation and vaporisation. Therefore, the contaminants in the wastewater generated from industrial activity need to be treated extensively. There are few method of treatment available which are summarized in table 2.2.

Ince & Kaplan Ince, (2020) claimed that the main source of environmental pollution is from the industrial and agricultural activities. Industrial effluent generated from electroplating and metal surface treatment contain high amount of heavy metals such as cadmium, zinc, lead, chromium, nickel and copper. Another industrial activity that generate significant amount of heavy metals include tin, lead and nickel are printed circuit board (PCB) production. In textile industry, heavy metal such as lead, chromium, cadmium and copper are also generated for production of colour pigments. Akpor et al., (2014) reported that the most common heavy metals found in the wastewater are arsenic, cadmium, chromium, copper, nickel, silver and zinc. It can be said that various of industrial activities may generate significant amount of heavy metal which can be harmful to the environment and human society.

2.1.1(a) Cadmium

Cadmium can be found in some soils. However, through mining and smelting, cadmium can be found at higher concentration than normal (Khaled & Mustafa, 2015). The acceptable amount of concentration based on the Environmental quality of Malaysia (Industrial effluent) is less than 0.02 mg/L.

2.1.1(b) Lead

Lead can be found in many types of industrial activities including smelting, battery manufacturing and electroplating. It also can be obtained naturally in soils. Lead contamination can adversely affect health by causing abdominal pain and memory problems. The acceptable amount of concentration based on the Environmental quality of Malaysia (Industrial effluent) is less than 0.5 mg/L.

2.1.1(c) Copper

Copper can cause Alzheimer's disease if directly ingested (Abedi Sarvestani & Aghasi, 2019). Copper can be found in electric and electronic industries which is used for cable and wire manufacturing. The acceptable amount of concentration based on the Environmental quality of Malaysia (Industrial effluent) is less than 1 mg/L.

2.1.1(d) Arsenic

In industrial activities, arsenic can be found through mining and smelting activities. Its toxicity can result to chronic to the bone marrow and damage to neurological system (Ratnaike, 2003). The acceptable amount of concentration based on the Environmental quality of Malaysia (Industrial effluent) is less than 0.1 mg/L.

2.1.1(e) Nickel

In manufacturing industries, nickel is used for armor plating. It is also being used for batteries production purposes. It has been reported that nickel may cause cardiovascular and kidney damage (Genchi et al., 2020). The acceptable amount of concentration based on the Environmental quality of Malaysia (Industrial effluent) is less than 1.0 mg/L.

2.1.1(f) Mercury

Mercury has been widely used in industries for manufacturing of electrical equipment, batteries semi-conductors and medical appliances such as thermometer. Mercury can be very harmful if been exposed at an adequate time where it can cause brain and liver damage (Broussard et al., 2002). The acceptable amount of concentration based on the Environmental quality of Malaysia (Industrial effluent) is less than 0.05 mg/L.

2.1.1(g) Chromium

Chromium is important in electroplating, tanning, printing and dyeing industries. It is also important in maintaining the long life of electrode metals as it provides a layer for protection purposes. Handling of chromium must be carried out properly to prevent any pollution form happening as it can cause nasal ulcer and cancer (Shekhawat et al., 2015). The acceptable amount of concentration based on the Environmental quality of Malaysia (Industrial effluent) is less than 0.05 mg/L.

Table 2.1 Health effect caused by the heavy metal

Heavy metal	**Toxicities**	**References**
Mercury	Damage to brain, liver, kidney	(Broussard et al., 2002)
Lead	Damage to nervous system, kidney, brain and cause anemia	(Hsieh et al., 2017)
Copper	Liver cirrhosis, Tyrolean infantile cirrhosis and altered structure of brain and liver	(Uauy et al., 2008)
Cadmium	Damage to kidney, bones and liver	(Nordberg et al., 2018)
Chromium	Bronchial asthma, lung, nasal ulcers and cancers and skin allergies.	(Shekhawat et al., 2015)
Nickel	Allergy, cardiovascular and kidney damage	(Genchi et al., 2020)
Arsenic	Chronic to bone marrow and damage to neurological system	(Ratnaike, 2003)

2.1.2 Method on the removal of heavy metals

Removal of heavy metal in the industrial wastewater has been widely studied to ensure the quality of the discharge effluent is comply to the standard percentage. There are several methods available for the removal of heavy metals. However, different methods have different percentage of removal. Table 2.3 shows the method on the removal of heavy metals.

Table 2.2 Methods on removal of heavy metals

Heavy metal	Removal method	Conditions	Removal efficiency (%)	References
Lead	Electrolysis	Anode: Platinum Cathode: carbon steel	94.71	(Santos et al., 2016)
	Chemical precipitation	Precipitant: Lime Ph: 7-11	99.37	(Chen et al., 2009)
	Floatation	Frother: Octadecylamine pH: 10	100	(Aldrich & Feng, 2000)
	Ion exchange	Resin: AMBERJET 1200 Na	99	(Zewail & Yousef, 2015)
	Membrane filtration	Membrane: Reverse osmosis	100	(Dialynas & Diamadopoulos, 2009)
Mercury	Ion exchange	-	98.56	(Oehmen et al., 2006)
Copper	Electrolysis	Anode: Platinum Cathode: carbon steel	96.19	(Santos et al., 2016)
	Chemical precipitation	precipitant: sulphide pH: 6	99.99	(K. Singh et al., 2017)
	Flotation	Frother: Ethanol and methyl isobutyl carbinol pH: 4-10	90	(Polat & Erdogan, 2007)
	Ion exchange	Resin: INDION225H	-	(Thakare & Jana, 2015)

		pH: 6.3-6.5		
	Membrane filtration	Membrane: reverse osmosis	49	(Dialynas & Diamadopoulos, 2009)
Cadmium	Electrolysis	Anode: Platinum Cathode: carbon steel	94.07	(Santos et al., 2016)
	Sorption	Material: 0.05 g of ceramic Contact time 16 hr Metal concentration: 2.5 ppm	99.6	(Arenas et al., 2020)
	Chemical precipitation	precipitant: sulphide pH: 6	99.88	(K. Singh et al., 2017)
	Floatation	Frother: Tea saponin	89.95	(Blöcher et al., 2003)
	Ion exchange	Resin: sargassum muticum loaded with calcium pH: 5	-	(Carro et al., 2015)
Chromium	Chemical precipitation	precipitant: Calcium hydroxide pH: 8.7	99.97	(K. Singh et al., 2017)
	Floatation	Frother: Ethanol and methyl isobutyl carbinol pH: 10	90	(Polat & Erdogan, 2007)
	Membrane filtration	Membrane: reverse osmosis	89	(Dialynas & Diamadopoulos, 2009)
Nickel	Chemical precipitation	Precipitant: Alkali pH: 2.5	98.4	
	Ion exchange	Resin: AMBERJET 1200 Na	98	(Zewail & Yousef, 2015)
	Membrane filtration	Membrane: reverse osmosis	100	(Dialynas & Diamadopoulos, 2009)
Arsenic	Ion exchange	-	98.56	(Oehmen et al., 2006)
	Membrane filtration	Membrane: reverse osmosis	100	(Dialynas & Diamadopoulos, 2009)

2.2 Lead as pollutants in industrial sources

Lead is highly harmful and toxic metal element that has been used extensively for many applications. Lead is a metal element that is silvery and bluish in colour that exists in small amount in the earth's crust. Lead also is a naturally occurring metal element. However, high exposure to lead can happen due to the human activities such as manufacturing, mining and fossil fuels. Lead has been widely used in various type of industries. Tchounwou et al., 2012 reported that lead is now used to produce lead-acid batteries, ammunitions, pipes and machine to protect X-rays. Exposure of high lead toxicity to the plant can bring harm to the growth of the plant by increase the rate of yield of reactive oxygen species (ROS) which result to damage to the lipid membrane of the plant that can permanently damage the photosynthesis and chlorophyll processes and inhibit the growth of the plant (Jaishankar et al., 2014). Lead also can cause negative effect to human if exposed to high concentration. Tchounwou et al., 2012 reported that lead exposure to children can cause poison to blood, lack of intelligence, lower intelligence quotients, weaken the nervous system that result to behavioural disorder.

There are various manufacturing industries that generate significant amount of lead contaminant including manufacturing of paint, batteries, cable sheaths, machinery and shipbuilding. Lead contamination in soil is mainly happen in the region where mining activity were occurred. High lead concentration also can be obtained in the untreated industrial effluent wastewater. According to the World Health Organization (WHO), the maximum allowable amount of lead in wastewater given by Environmental Protection Agency of USA (EPA) is 0.05 mg/L. However, lead concentration in the industrial wastewater is high which is approximately around 200-500 mg/L. Thus, the concentration of the lead ions (II) need to be lowered to around 0.05 – 0.1 mg/L before discharging to the sewage system. Few treatments can be performed to counter the lead ions contaminations including adsorption, precipitation, coagulation, ion exchange, cementation, electro-coagulation and reverse osmosis.

2.2.1 Methods on lead removal treatment

In this section, the effectiveness on the removal of lead were reviewed by discussing the removal efficiency of lead through a few treatments. There are several treatments studied which are chemical precipitation, electrolysis, floatation, ion exchange membrane filtration and adsorption.

2.2.1(a) Chemical precipitation

In this treatment, precipitates will form when a correct amount of chemicals are added due to the reaction between the chemicals and the heavy metal contained in the wastewater. The precipitate will be removed through sedimentation process and the water treated is decanted (Djedidi et al., 2009). There are few categories that are under the chemical precipitation which are hydroxide precipitation and sulphide precipitation.

In hydroxide precipitation method, the hydroxide added into the wastewater will react with the heavy metal present and thus, metal hydroxide will be produced. Removal of lead and few other heavy metals through chemical precipitation has been studied by Chen et al., (2009),where lime was used as the precipitant. Lime was chosen due to the low cost and addition of fly ash will increase the lime precipitation. The suspension will then be exposed to carbon dioxide gas. Through this method, the efficiency of lead removal increases when the fly-ash-lime carbonation was performed. This treatment results to reduction of the heavy metal concentration to the allowable limit. The removal of lead (II) ions was achieved between pHs 7 and 11 and the removal efficiency reported was up to 99.37-99.69%.

2.2.1(b) Electrolysis

Electrolysis is an effective method for removal of heavy metals compared to conventional technique as no chemical input needed and there will be no sludge generated after the treatment (Santos et al., 2016).This treatment works by introducing the electric charge into the solution containing heavy metal. In this process, the electric is conducted through the cathode and anode which have been immersed into the solution. The positively charged heavy metal will deposited on the cathode which result to the separation of the heavy metal ion from the solution. Santos et al., (2016), has used electrolysis method in removing lead from the solution where the platinum was used as anode and carbon steel was used as cathode. The solution was continuously stirred and kept at temperature 25^{o}C. The voltage supplied was set to 20-30 V. Results showed that the removal efficiency for lead is 94.71%.

2.2.1(c) Floatation

Floatation has several advantages including selective metal ion recovery, low amount of sludge generated and effective in heavy metal removal (Rubio et al., 2002). Ion floatation is also a promising method for treating a solution as it can handle large volume of aqueous solution (Yuan et al., 2008). In this treatment method, collector is needed as it transports non-surface active colligend ions of the different charge from a bulk solution to the solution-vapor interface. Studies carried out by Yuan et al., (2008), where removal of lead is performed by floatation method with plat-derived bio-surfactant tea saponin. The parameter that affecting the floatation process are initial solution pH, the collector to heavy metals ratio and the strength of the NaCl ion. The highest removal of lead is 89.95% at 3:1 for ratio of collector to metal. In this study, it was found that the affinity of lead towards the tea saponin is the highest compared to cadmium. The combination of the ion floatation and the biosurfactant is a good approach as the material used is environmentally friendly. The high affinity of the biosurfactant towards the heavy metals make it a better choice to be used widely in treating heavy metal contaminated soils (Yuan et al., 2008).

2.2.1(d) Ion Exchange

Ion exchange treatment generate low volume of sludge and the resin is easily recovered by regeneration process (Abo-Farha et al., 2009). This treatment works when the transferring of ions to the solid matrix occur which result to release of different type of ions but of the same charge (Zewail & Yousef, 2015). Few advantages of this treatment are the recovery of the metal value, selectivity, less volume of sludge generated and able to meet the specification discharge. In industry application, the treatment is performed in the fluidised bed or fixed be reactor (Zewail & Yousef, 2015).

Studies performed by Zewail & Yousef, (2015) on the removal of lead ions by ion exchange method in batch conical air spouted bed was performed. The resin used in this technique is AMBERJET 1200 Na. In this study, several parameters that affecting the removal efficiency of lead was investigated. The removal efficiency of lead increase as the air spouting velocity increase to a certain limit. Beyond the limit, the air spouting limit does not give any effect to the removal efficiency. In addition, the resin used has high affinity towards the lead. The highest removal efficiency of lead reported in Zewail & Yousef, (2015) is 99%.

2.2.1(e) Membrane filtration

There are several advantages for membrane filtration as compared to the conventional technique which are it gives high separation efficiency, no phase change involved, save energy consumption and can easily scale-up and sustainable (Gao et al., 2014). The removal of the heavy metals includes few of the techniques which are ultrafiltration (UF), reverse osmosis (RO) and nanofiltration. The driving factor for reverse osmosis (RO) is pressure. Work investigated by Dialynas & Diamadopoulos, (2009), shows that the lead ion can be removed completely by using reverse osmosis method. In this study, a pilot-scale membrane bioreactor (MBR) was used.

2.2.1(f) Adsorption

Adsorption is a process where the molecules of gas or liquid adhere at an adsorbent surface. The molecules that are adsorbed to the solid surfaces are called adsorbate while the solids are called adsorbent. There are few common examples of adsorbent available such as clay, silica gel and colloids. The capability of the activated carbon to adsorb high amount of contaminants make it becomes promising to be used as adsorbent. The effectiveness of the adsorption process depends on few parameters such as pH of the solution, temperature of the solution, concentration of adsorbate and adsorbent and contact time.

2.3 Activated Carbon

Activated carbon is an adsorbent that is large in surface area with a great amount of porous structure formed on it. Activated carbon is utilised as an adsorbent because of the effectiveness for adsorbing a broad types of contaminants in liquids or gases (Koehlert, 2017). Activated carbon has been applied in various type of industries for the removal, recovery, separation and alteration of different compounds in gas and liquid phases (Heidarinejad et al., 2020). Adsorption technique by using solid substance is more favourable and common to be used at the industrial scale (Crini et al., 2019). There are wide range of sources that are available for the preparation of the activated carbon such as coal, wood biomass waste, industrial waste and plant remains.

On a commercial quantity, the usual sources for production of activated carbon is wood, anthracite and bitumen charcoal, lignite, peat shells and coconut (Heidarinejad et al., 2020). Usage of renewable sources as a raw material to produce activated carbon can be beneficial for economy and environment as it is cost-effective and sustainable. Renewable sources including biomass, polysaccharide and microorganism that contain carbon as precursor can be used to produce activated carbon (Selamat et al., 2020). There are biomass that are available for production of activated carbon such as sugarcane bagasse, coconut shell, peanuts shell, almond shell, sunflower seed and rice husk (Selamat et al., 2020). The carbon contain in these biomass exist as precursor were utilised by researchers and further processed it into adsorbents through few process includes char production and activation (Selamat et al., 2020). Table 2.4 shows various type of available renewable sources for processing of activated carbon.

Table 2.3 Various type of available renewable sources for processing of activated carbon

Raw material	**References**
Vine shoots	(Corcho-Corral et al., 2005; Manyà et al., 2018)
Grape bagasse	(Demiral & Güngör, 2016)
Almond shell	(Omri et al., 2013)
Sugarcane bagasse	(Guo et al., 2020)
Cherry stones	(Olivares-Marín et al., 2009)
Apricot stones	(Schrder et al., 2011)
Orange peel	(Moreno-Pirajján & Giraldo, 2012)
Coir pith	(Santhy & Selvapathy, 2004)
Coconut tree sawdust	(Kadirvelu et al., 2003)
Sago waste	(Kadirvelu et al., 2003)
Maize cob	(Kadirvelu et al., 2003)
Banana pith	(Kadirvelu et al., 2003)
Mangrove barks	(Oo et al., 2009)
Maize tassel	(Moyo et al., 2013)

2.4 Activation method of activated carbon

Activated carbon is a common adsorbent used in various applications especially in the wastewater treatment industries (Saleem et al., 2019). The preparation of the low-cost adsorbent involves a raw material such as agricultural waste as precursor. The raw material will be crushed, milled, briquetted or mixed with extruder before undergo activation process (Koehlert, 2017). This pre-processing steps are intended to minimize the size, form and other features (Koehlert, 2017). Production of the activated carbon involves two-level process which are carbonization and activation (Singh & Kalia, 2017). The operating condition of the carbonization process take place at 450^{o}C to 600^{o}C (Singh & Kalia, 2017). The reaction involves decomposition of the fresh material to hydrocarbon compounds and formation of products that are carbonaceous (Singh & Kalia, 2017). The carbonization method is performed to develop initial porosity (Yahya et al., 2015). The activated carbon is further processed to form pores structure that contributes to the development of small solid space in the activated carbon (Heidarinejad et al., 2020). Generally, the activation process is prepared in two methods which are physical and chemical.

2.4.1 Physical activation

Activated carbons may be produced in a physical method either through direct carbonization-activation method or through firstly, carbonization process of biomass and then activating the bio-chars into activated carbon (Bergna et al., 2018). The type of methods applied depend on the characteristics of the activated carbon (Bergna et al., 2018). Commercially, the method used in physical activation involves two step processes (Yahya et al., 2015). The first step is activation that is performed at temperature of 673-973K (Bergna et al., 2018). During this process pyrolysis gases is mixed with pyrolytic oil which results to remove most of the volatile components (Bergna et al., 2018). For the second stage of the process, the carbons are activated at operating temperature of 973-1173K and combined with activating agents such as steam and carbon dioxide (CO_2) or gaseous and steam mixture (Bergna et al., 2018; Yahya et al., 2015). The application of CO_2 as the activating agent is preferable as it is clean, uncomplicated to control and the process is easy to handle at temperature of 800°C due to the slow reaction rate (Yahya et al., 2015). It also been reported that high uniformity of pore can be obtained when using CO_2 compared to steam (Yahya et al., 2015). The optimum condition of activation using CO_2 is at temperature of 800°C for 1 hour while for steam the temperature is at 700°C for 1 hour (Pallarés et al., 2018).

2.4.2 Chemical activation

Moyo et al., (2013) has studied the performance of the maize tassel based activated carbon by using sulphuric acid as the chemical activation for the removal of lead (II) ions by varying few variables such as initial metal ions concentration, contact time, adsorbent dosage and pH. It was found that the adsorption capacity based on the Langmuir isotherm is 37.31 mg/g (Moyo et al., 2013).

Chemical oxidation is also known as wet oxidation (Yahya et al., 2015). In this process, it involves impregnation of strong dehydrating agent and oxidants into the precursor. It is then been washed to produce activated carbon. The exact choice of dehydrating agent as well as the activation process condition is important as it will determine the quality of the activated carbon production. The interaction of the various type of dehydrating agent with the precursor will affect the action of the adsorption process. The common operating temperature used in this process is at 450-600°C (Yahya et al., 2015). The dehydrating agents that are commonly used are zinc chloride, phosphoric acid, sulphuric acid, sodium hydroxide and potassium hydroxide (Yahya et al., 2015).

2.4.3 Activated carbon produced from different chemical agent

Previous studies performed by Kongsuwan et al., (2009) was *Eucalyptus camaldulensis Dehn* bark used as the raw material and using phosphoric acid as the chemical activating agent.

It has been reported that the optimum pH for the adsorption process is at 5. The maximum sorption capacities for copper (II) and lead (II) reported are 0.45 and 0.53 mmol g^{-1} respectively. Kongsuwan et al., (2009) also reported that the activated carbon produced has great amount of functional group binding sites for lead (II) compared to copper (II). This was supported as the *b* constant that indicates the bonding energy of sorption for copper (II) is higher than lead (II). This indicates that the chemical and physical affinity of lead (II) with the activated carbon is stronger than copper (II).

Studies by C. K. Singh et al., (2008), reported that activated carbon derived from Tamarind wood was activated with sulphuric acid and it was found to be effective for removal of lead (II) at condition of 3 g/l of initial adsorbent dose and pH 6.5. The BET surface area and total pore volume of the adsorbent was 612 m^2/g and 0.508 cm^3/g respectively (C. K. Singh et al., 2008). The studies also claimed that the high removal of lead (II) up to 97.95 % that make the Tamarind wood activated carbon as the best adsorbent for lead (II) (C. K. Singh et al., 2008).

Additionally, derivation of activated carbon from mangrove propagule waste was activated by using phosphoric acid as the dehydrating agent (Astuti et al., 2017). Astuti et al., 2017 also reported that the surface area of the activated carbon increase from 187.18 m^2/g to 267.45 m^2/g when using chemical activation agent and new pores also formed on the adsorbent.

Li & Wang, (2009) in their studies prepared activated carbon from *Spartina alterniflora* by using phosphoric acid activation for lead (II) removal from dilute aqueous solution. In their studies, it was reported that pH had a big role in the adsorption process (Li & Wang, 2009). The optimum pH of the adsorption was 4.8-5.6 with maximum adsorption of lead (II) at 99 mg/g (Li & Wang, 2009).

Another type of biomasses used is *Jujube* stoned performed by Bouchelkia et al., (2016). In their studies, the *Jujube* stones used was chemically activated by using sulphuric acid to remove lead (II). It was reported that the adsorption capacity of lead (II) was 71.43 mg/g by using Langmuir isotherm model. The results revealed that activated carbon derived from *Jujube* stones could be considered as a good potential to be used for the removal of lead from wastewater.

2.4.4 Physiochemical activation

Physiochemical activation is a process where physical and chemical activation are combined. Generally, the raw material will undergo carbonization process at certain operating condition and proceed to the next stage where it is impregnated with the dehydrating agent at desired impregnation ratio. It is then been dried at high temperature and held under steam activation or by using CO_2. The operating condition for the steam activation at temperature of 601 to 799°C (D. et al., 2013) while for CO_2 activation is in a range of 400-800°C (Sutrisno & Hidayat, 2015).

2.4.5 Microwave irradiation

Commonly, the activation procedure is conducted by using conventional furnace. Usage of conventional furnace has some limitations such as the heat energy required is high as the heat is used to heat the elements to the reactor then, to the sample. Besides, the high consumption of heat energy will also result to high production cost (Lam et al., 2017). Thus, microwave irradiation method is more preferrable for activation of the char. It possesses few advantages such as the heating can be controlled accurately and it is flexibles as it can be turned on and off at instant time. In addition, microwave irradiation able to serve an efficient heating process by rapidly retain a high temperature in fer minutes compared to conventional furnace (Wan Mahari et al., 2016). Microwave irradiation also able to has selective heating mechanism. This is due to different type of materials have different reaction to the microwave irradiation (Wan Mahari et al., 2016). The material can be classified into different types which are conductors, insulators and adsorbers.