CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Environmental pollution is one of the most important problems nowadays. The contamination of water resources by hazardous pollutants like dyes, heavy metals and bacteria has been attracted recently due to their poisonous activity. Wastewater is very harmful to the human body and environment due to the toxicity of heavy metals and dyes (Abdel-Ghani & Elchaghaby, 2007; Horne, 2013). The wastewater contains various types of pollutants, dye is one of the most contaminants (Kobylewski & Jacobson, 2010). Methylene blue is an organic compound ($C_{16}H_{18}ClN_3S_3H_2O$) and is very toxic to human beings and the environment (Choi & Yu, 2019; Mohammadi et al., 2017). It has several harmful effects on human beings including increased heart rate, vomiting, shock, jaundice, and tissue necrosis (Sharma et al., 2010; Khodaie et al., 2013). Generally, heavy metals entered into the water system from many industries. Cadmium (Cd) is released from zinc melting and paint sludge industries. Lead is released from lead batteries and ceramics. Metal ions are important pollutants due to their toxicity (E. Demirbas et al., 2004). Toxic heavy metals are very dangerous for non-biodegradability. These all gather in living organisms causing disease and illnesses (Wan Ngah & Hanafiah, 2008). This poisonousness may influence nervous systems and other vital organs (Ahmaruzzaman, 2011).

2.2 Sources of Wastewater

Generally, 2 million tonnes of household, industrial, hospital, and agricultural waste are entered into the water system per day. The synthetic dyes are produced from many industries about 7×10^5 tons per year. The UN estimates that the waste water produced is about 1,500 km^3 per year which is six times more water than exists in all the rivers.

The wastewater produced from different industries is a major cause of environmental pollution.

The drain water of the household contains various contaminants such as oxides of salts, detergent, oil, grease etc. In the water cycle, there are several ways by which the earth loses water. One of the ways by which water comes back to earth is through rainfall. At this stage, the water is relatively clean without acid rain and can be collected for use with minimal capital investment. However, allowing rainwater to flow over the surface of the earth causes environmental disasters in the form of flooding, soil erosion etc. Generally, it is possible to harness it for use in households, agriculture, and livestock.

Wastewater also comes from hospital waste. It may contain water from poisonous blood, unnecessary medicines, body fluids, and human excreta. This wastewater may be consumed directly into major watersheds. It can have serious impacts on the environmental ecosystem. This also can affect public health. Even hospital wastewater has a abolished effect. It may create and prolong epidemics (Rhodes et al., 2000). Wastewater comes from human activities and is polluted by a variety of poisonous substances. It harms the water environment. It contributes seriously to the pollution load of the receiving water bodies. For this reason, it increases the ecological risks. Alkaline chlorination is a common method for free cyanide from wastewater. Even chlorination of cyanides can produce toxic intermediates. It also can make toxic organo-chlorines. That's why it can destroy the normal ecosystem.

The industry of electroplating releases a huge quantity of wastewater. That is very harmful, having varieties of toxic metals. Some of these are nickel, copper, lead, cadmium, and suspended solids. The characteristics of electroplating wastewater depend on the type of plating industry. It differs from plant to plant. There are some techniques for removing heavy metals. But it is costly, slow, and not easily bearable. It has some side effects on the human body. Most of the industry's wastewater comes from rinse waters. This type of water also contains a cleaning solution. Most of the basic solutions have soaps, grease as well as oil. Pickling wastewater is made of acidic rinse

water and metallic salts. Plating baths wastewater containing copper, nickel, and lead etc. These metallic wastewaters are poisonous. It may be acidic or basic.

The electroplating industry expresses a vital role for improving the metal manufacturing sector. It has been increasing from small to medium industries. It is mainly shown in rising countries such as Malaysia, Thailand, and Bangladesh etc. There are over 60,000 varieties of electroplating units. It is mainly represented by small-scale units. Those were old technologies where unskilled workers were involved. It is located in unplanned and illegal areas with the lowest facilities (Upadhyay, 2006).

2.3 Sources and Effects of Heavy Metals to Human body & Environments

Some heavy metals are needed for human beings. Metal compounds are also needed for soil or land to fertilize plants. Fertilizers as a metal compound can be used in soils. So, Metal adsorption methods are essential to define metal availability to the soil. The most common sequences were Pb > Cr > Cu > Cd > Ni > Zn. Here, some metals were strongly attached with soil like lead and copper. On the other hand, cadmium, nickel were the minimum attraction with soil (Gomes et al., 2001). The metallic cadmium attaches in ores composed. Cadmium is also part of a polyvinyl chloride (PVC) product. Generally, cadmium is used as an anti corrosion agent. Metal alloys and pigments are produced using chromium. Chromium can destroy the lungs of human beings. Chromium is also used in paints, cement and other materials. There are some industries like chemical, steel and electroplating for producing varieties of metal. Lead metal comes from coal mines. It causes headaches and abdominal pain in human beings. Lead exposure in men may reduce intellectual capability. Cadmium exposure may cause kidney damage. Copper may be found in mushrooms (Yu et al., 2000) but it can damage the stomach and kidney. Heavy metals can cause damaging health problems (Järup, 2003). Any metal may be considered as a “pollutant”. High toxic metals are included such as lead, cadmium, copper, and nickel etc. Other hand, aluminium, cobalt, manganese etc. are less toxic (Singh et al., 2011).

Heavy metals are very hazardous elements. It has a high atomic weight. Human beings need several bit metals. But twelve metals are toxic. Some of these are nickel, copper, and lead. It may reduce the metabolism system. Toxic metals may cause health effects on the human body like that respiratory system and cancer. It can accumulate in the body by taking contaminated food. After entering the body, it is stored in tissue. That's why human beings are faced with chronic health problems. This study is discussed about four hazardous metals. Such are cadmium (II), copper (II), lead (II), and nickel (II). These are discussed below.

Cadmium metal is also listed by the Environmental Protection Agency (EPA) as pollutants. The compounds of cadmium are very poisonous elements for the human body. Pneumonia disease can be shown by severe toxicity of cadmium. For this reason, human beings suffer from diarrhea due to toxicity of cadmium. Kidneys may be damaged also for this toxicity. Enzymes system is affected by this metal. Prolonged exposure to cadmium causes lung, kidney and hematopoietic system damage. Cadmium has shown strong evidence of cancer. Fish is affected by this metal. It is the only element that stores the rising age of an animal. The permissible limit of cadmium in drinking water according to WHO is < 0.005 mg/L.

Copper is necessary for the nutrients of human beings. Every day needs 0.9 mg of copper recommended by Daily allowance (RDAS). Several body proteins contain some copper. Copper can cause vomiting & diarrhea. Only two grams of this metal is enough for anemia. It can damage the liver that can cause death. It has both short & long term effects. In mammals, over exposure of this metal may destroy the kidney (Monser & Adhoum, 2002). Fishes can also be affected by copper.

There are 129 pollutants in the environment recorded with EPA. One of them is chromium. Basically, it has two major oxidation positions. Such as Cr (III) & Cr (VI). More stable state is Cr (III). It is an important nutrient for the body. It needs a small amount. Chromium maintains the glucose metabolism process. But Cr (VI) is non-biodegradable (Chen et al., 2007). Though the toxicity of Cr (III) is lower. It may cause allergic problems.

Kidney & liver can be damaged by Cr (VI) elements. A long-time contact can affect the respiratory system. The discharge of Cr (VI) is controlled to < 0.05 mg/L. Chromium also discharges 0.1 mg/L to inland surface waters by the US EPA. Where the whole chromium is controlled to be released at < 2 mg/L (Baral & Engelken, 2002). Chromium (VI) is also converted to Cr (III) through two mechanisms. Such as (1) direct reduction by contact with the electron-donor groups of biosorbent. Another one (2) indirect technique containing three phases of binding of chromium (VI) ion to positively charged adsorbent. It is converted to Cr (III) and then releases the created Cr (III) ions (Abdolali et al., 2014).

The nickel (Ni) needed for dietary requirements of human beings. But nickel can be poisonous in more dosage. Generally, the body contains about 100 mg of nickel. It may cause gastrointestinal symptoms. Such as nausea and vomiting. It also causes headaches. The pulmonary and digestive tract of humans can be affected by nickel. It also causes respiratory tract cancer due to over dosage 1 mg of Ni/ L. Long time contact of this element can affect bronchitis and lung function. Lung and immune systems can be affected by this metal (Ni) (Irina Lehmann, 2011).

Lead that is available in contaminated water comes from various industries like that battery, glass manufacturing, metal plating and production of lead additives from gasoline (Momčilović et al., 2011). Its poisoning is irritability and the nervous system. Encephalopathy of lead is considered by insomnia and anxiety. The baby can be affected by toxicity of this lead metal. Even intellectual capacity can be damaged by lead metal. It can cause damaging health effects on human body (Järup, 2003).

Generally, metalloid species are known as “contaminants”. Metalloids include lead, mercury, arsenic, and silver. Other sides, cesium, strontium, and uranium are less toxic (Singh et al., 2011).

2.4 Environmental Pollution and Health Problems

Generally, heavy metals are accumulated in the food chain and environment. Electroplating industries discharge wastewater into water bodies and this type of wastewater contains toxic metals and other pollutants which are hazardous for human beings. This wastewater has organic matter which reduces oxygen from this system. Even water contains inorganic matter which can change water quality as unhealthy. There are some metallic and nonmetallic ions. Such as lead, nickel, cadmium, sulphide, and cyanide etc. Oil and grease reduce the streams hideous with their own-purification. Electroplating wastewater is alkaline in nature. In some counties, people have baths in rivers. But they smell bad from this water. It makes polluted water bodies. For this reason, people cannot live well because of the pollution of nearby polluted rivers.

There are many microorganisms in wastewater. Generally, wastewater contains different types of micro-organism such as *E. coli*, *Pseudomonas aeruginosa*, *Aspergillus niger* etc. For this reason, humans suffer from Malaria, Cholera, Typhoid, Viral hepatitis, skin diseases etc.

2.5 Methods of Wastewater Treatment

There are many methods for purifying polluted water. Several common processes are mentioned below.

The Ion exchange method is one kind of process which has some advantages and disadvantages. This process happens by the ion exchange for the removal of pollutants. It occurred between two phases such as exchange medium & wastewater. Organic or inorganic polymer resins are used for this system. This type of resins may be regenerated. It is an effective method but it cannot be used broadly due to the costly process. It has also another disadvantage that its resins absorb toxic chemicals. It needs to be disposed of (Upadhyay, 2006).

Flocculation can be used for elimination of suspended particles from contaminated water. It is easily removed as floes. Flocculation is often preceded by coagulation. With

adding a coagulant, substances are accumulated. It can be converted from microscopic particles into larger floes. The most commonly used for coagulation processes are aluminum sulphate. Mostly synthetic polyelectrolytes and clay is used as coagulant aids (Semerjian & Ayoub, 2003). The disadvantage of this process is costly operation and maintenance cost high.

Wastewater can be treated effectively by chemical precipitation method. This type of process is used hydroxide, carbonate or sulphide reagents. Generally, metals may be precipitated as hydroxides with controlling pH. After completing process, it is eliminated from system with filtration process. However, this method is not effective enough. Another problem is that chelated metal ions can not be eliminated from the system by this process. This is an incomplete method and has some side effects. It can produce huge sludge that requires to be removed (Upadhyay, 2006).

Evaporation is a very costly method. It can be applied to regenerate metals. There are two types of evaporation stages. Such as Single and multiple stages. Due to high cost of equipment this method is not commonly used (Upadhyay, 2006).

Biosorption is a biological sorption method. There are used live or dead microorganisms. Here functional groups of surfaces can bind metal. It is a more cost effective method than others. But it takes a long time to eliminate pollutants. The regeneration process is not possible for reuse.

2.5.1 Adsorption

This process is one of the more effective methods for wastewater treatment. It is the surface phenomenon. Adsorption is also defined as the "increase in concentration of a particular component at the interface between two phases". The substance that is removed from the liquid phase is called the adsorbate. Besides, the adsorbent is the solid, liquid or gas stage onto which the adsorbate gathers. There are mainly two type's adsorption processes such as: physical adsorption and chemical adsorption. It is a cost effective and simply available method. The adsorption process has three main steps.

Such as (1) the first step is the transport of the adsorbate to the outer surface of the adsorbent. It is called film diffusion. (2) The second step, known as internal diffusion involves the transport of the adsorbate to the interior sites by diffusion. (3) The third step is the adsorption of the solute on the active sites on the interior of the pores.

2.5.1.1 Physical adsorption

In physical adsorption the process does not transfer electrons. Physical adsorption is one kind of electrostatic interaction. It happens between ions in solution and cell walls. The interactions are fully reversible which is not site specific. Physical adsorption method includes Van der waals' forces of attraction. It is not reliant on cell metabolism. Tsezos verified that uranium biosorption by fungal biomass. It is built on physical adsorption. It has assumed that uranium, and copper biosorption by dead biomass of fungi and yeast. *Rhizopus arrhizus* can adsorp cadmium, and lead by this process.

2.5.1.2 Chemisorption

Chemisorption is one kind of chemical interaction. It happens between adsorbent and adsorbate. The attraction force is stronger than the physical process. It is irreversible. Chemisorption is site specific. Physical adsorption happens at low temperatures. But chemisorption occurs at high temperatures. Sometimes both the phenomena may occur at the same time.

2.6 Adsorption of Activated Carbon

Adsorption is a vital alternative process to remove contaminants from wastewater. The Absorption process can be occurred by two kinds of biomass. Suca has non-living biomass and living biomass. Rice husk, coconut coir, and potato peel can be used as a non-living adsorbent. On the other hand, microbial cells, fungi, and yeast may be used as a living adsorbent (Chen & Wang, 2008). This type of adsorption is the most effective

method for removing pollutants. This method is very popular due to simplicity, availability and cost effectiveness (Monser & Adhoum, 2002). The adsorption capacity is based on its high action, surface area and similarity of its shape (Yahya et al., 2015). Activated carbon fit for removing contaminants from water, air, and gas streams (Jain et al., 2016); (Alslaibi et al., 2013); Nguyen et al., 2013). It encouraged the attention to exploit raw materials that are cheaper and abundant in nature. When cheap precursors are used, the production cost and the disposal problem are reduced (Al-Qodah & Shawabkah, 2009).

Activated carbon is a monumental porous carbon material (Ahmad et al., 2012). It plays a vital role in various sectors. It possesses a great surface area ranging from 1000 m^2/g to 2800 m^2/g. It is best used for the adsorption and storage applications due to its highly porous material (Alabadi et al., 2015). Quality of adsorbent depends on its pore size. Pore size can be defined in three names using IUPAC classification. They are: micropores (when pore width < 2 nm), mesopores (when pore width 2 nm - 50 nm) and macropores (when the pore width > 50 nm) (Yahya et al., 2015). There are two forms of commercial activated carbon such as: powder and granular. Powdered activated carbon is used as liquid media and sizes of 15 – 25 μm. In contrast, granular form is mainly used both in liquid and gas applications. Both are largely used in medicine (Ilomuanya et al., 2017), pharmaceutical (Nguyen et al., 2013; Jodeh et al., 2016), wastewater treatments (Bonvin et al., 2016).

Most of the water treatment processes are very costly globally (Joshua & Vasu, 2013). Therefore, it is essential to find natural alternatives that are cost effective and available. There are some essential agricultural products such as rice husk, coconut coir, corn cobs, neem bark and *Moringa oleifera* bark for purification of contaminated water. *Moringa oleifera* (*MO)* is one of these best alternatives for wastewater treatment (Bhuptawat et al., 2007). Leaves and seeds of *MO* are very frequently used for water treatment (Bichi, 2013). *Moringa oleifera* has no side effects. It is non-toxic and ecological material (Onyuka et al., 2013). *MOCR* (*Moringa oleifera* cake residue) don't need further preparation for the water purification process (Arnoldsson et al., 2008). *MO* seeds have coagulant properties. *Moringa oleifera* remove turbidity and also have antimicrobial properties (Meneghel et al., 2013).

2.7 Adsorbents from Agricultural by-Products

There are lots of adsorbents for purifying wastewater. Most favourite adsorbents are activated carbon, synthetic polymeric and silica-based adsorbents. Most are not used widely due to high cost. Several developing countries are facing problems in wastewater treatment due to high cost. That's why, the effectiveness of low cost adsorbent is being studied widely for the cheaper and easily available. It also must be simple. So, activated carbon derived from natural by-products can be alternative effective adsorbents. Several researchers have produced activated carbon from different natural by-products such as orange peel (Khaled et al., 2009), coconut husk (Foo & Hameed, 2012), coffee husk (Ahmad & Rahman, 2011), black acacia bark wastes (Silva et al., 2018), and rice husk (Rahman et al., 2012).

2.7.1 Rice Husks

It is the by-products of the rice milling factory. It is the outer covering of rice grains. It contains 23 % of rice grain. China and India are the top rice producing countries. It can be used as a source of energy for boilers. It also used as a building

Figure 2.1 Rice paddy and husk

material, fertilizer and industries. However, in the local area, the excess rice husk has disposal problems. It contains SiO_2 in hydrated amorphous form like silica gel which is good as absorbent. Ajmal et al., (2003**)** showed about rice husks for elimination of Cd

(II) from polluted water. Acid modified rice husk was good adsorption for Ni (II) and Cd (II) where sorption of Cd (II) pH dependent. If the adsorbent particle size is reduced, the binding of metal ions increases where the surface area and binding sites increase. The affinity of activated carbon of rice husk is good for Pb adsorption. Tartaric acid modified rice husk (TARH) had the maximum removal abilities for Cu and Pb. The carboxyl groups on the rice husk were responsible for the removal of metal ions. The adsorption capacity of activated carbon increased due to the chemically activated with zinc chloride compared to using raw rice husk char (Ahiduzzaman & Sadrul Islam, 2016).

2.7.2 Coconut Coir

Coconut coir is an outer covering of coconut. It consists in lignin (16-45%), hemicellulose (24-47%), and pectin (2%) content (Conrad & Bruun Hansen, 2007). These compounds contain the carboxyl and phenolic groups which have the ability to bind metal (Conrad & Bruun Hansen, 2007). It is cheap and available in abundance in developing countries. There are top two producers such as India and Sri Lanka. They produce about 90% of coir fibre. It is available in Malaysia and Bangladesh. There are various names such as coir, coco peat, and coir dust. All of these are made of coconut fiber. This is the fibrous layer of the fruit. It is created by the extraction of the long fibers from the husk. It has the binding material that comes from the fiber fraction of the coconut husk (Vishnudas et al., 2005). However, the yield of fibre is 80-90 g out of 1000 g.

Figure 2.2 Coconut tree and coir

The coir pith has a discarding problem as it takes 20 years to decompose even though it is biodegradable. It has adsorbent properties and consists of 35% of husk. In 2001, coconut trees were being planted on about 151000 ha land for Malaysia. It was proved that coconut husk was being collected about 5,280 kg/ha every year (Tan et al., 2008). The activated carbon of coconut husk was used to remove phenol, acid red 27 dye and copper from wastewater (Phan et al., 2006).

2.7.3 Corn Cobs

Activated carbon of corn cobs was used in adsorbing heavy metals from a paint industry wastewater. According to (Demirbas et al., 2004), the study of adsorption dynamics describes the solute uptake rate and rate controlling step. It has comparatively great carbon content matched to others like rice husk, neem bark, and also a cheaper method for paint wastewater treatment for developing countries (Okafor et al., 2015). Paint industries are discharged effluents containing pigments, solvents and blotters. Generally, heavy metals are mainly used as pigment and blotters in paints. So, many researches had been conducted to find alternative adsorbents from agricultural wastes products like zeolite, rice husk, corn cob, and peat for paint wastewater treatment (Okafor et al., 2015).

Figure 2.3 Corn cobs and tree

2.7.4 Neem Tree

(Bhattacharyya & Sharma, 2004) studied uptake of chromium (VI) using neem leaf and got a novel adsorbent from this which can remove heavy metals of wastewater. The fine powder of activated carbon was found to remove chromium (VI) from water solution. (Venkateswarlu et al., 2007) studied elimination of chromium from a wastewater solution using neem leaf powder. In this investigation, powder form of neem leaf was used as an adsorbent for wastewater treatment. Pandhare & Dawande, (2013) studied that neem leaves can be used as cheaply adsorbents. It was used to remove impurities from effluents.

Figure 2.4 Neem tree and bark

2.7.5 *Moringa oleifera*

Moringa oleifera is the most important species of this family and multipurpose trees. It is available to the sub-Himalayan tracts of SouthEast Asia (Prabhu et al., 2011). *Moringa oleifera* can be used as an absorbent and coagulation (Prabhu et al., 2011). The seeds also have antimicrobial activity. The seeds of *Moringa oleifera* are conventionally used as a natural coagulant. It has strong coagulating properties. *Moringa oleifera* (*MO*) successfully eliminated the heavy metals from wastewater. Generally, 1% of *Moringa Oleifera* is sufficient to purify of Wastewater (Eman et al., 2014).

Figure 2.5 *Moringa oleifera* tree and bark

The activated carbon of *Moringa oleifera* has the ability to remove anionic surfactants from wastewater. So it has a promising future as a water treating agent. Polluted water is the derivative from agricultural and industrial activity. Nowadays in the era of globalization, many water treatment methods have been invented. But most of them require higher expenditure (Joshua & Vasu, 2013). Aluminum sulfate is used as an unadventurous chemical coagulant. But as an alternative natural coagulant, *Moringa oleifera* seeds can be used properly. The key goal of adsorption studies is to explore the effectiveness and cheaply available of *Moringa oleifera* for reducing pollutants from environmental pollution. Various parts of *Moringa oleifera* such as stem, bark, and roots have antimicrobial activities (Lockett et al., 2000). *Moringa oleifera* leaves possess antimicrobial and antioxidant properties due to phytochemical compounds such as saponins, flavonoids, tannins and other phenolic compounds. The

existence of pterygospermin compounds which act as potential antibacterial and fungicidal effects.

Moreover, polypeptides of adsorbents have bactericidal properties against many pathogenic bacteria (Lürling & Beekman, 2010). *Moringa oleifera* seed has cyano-bactericidal activity (Chumark et al., 2008). *Moringa oleifera* root aqueous extract shows activity against *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *E. coli*. (Raj et al., 2011).

2.8 Preparation of Activated Carbon

The preparation of activated carbons has two main steps. First one is the carbonization of the raw material. Second one is the activation of the char. It can be used for either physical or chemical activation (Alslaibi et al., 2013).

2.8.1 Carbonization

Rodriguez Correa et al. (2017) defined carbonization is a one kind of process where organic material can be converted to fundamental carbon at constant temperature under inert conditions. During this process, the volatile compounds are removed and char is formed. The produced char commonly has poor adsorption capability due to the poor porous structure. The reactions were usually complex. It happened concurrently at varying rates depending on type of organic materials (precursors), carbonization time and temperature involved. Normally, growing the carbonization temperature decreases the carbon yields (Ioannidou & Zabaniotou, 2007). Generally, the optimum carbonization temperature is in the range of 500 to 900 °C. The products of carbonization are chars, gas and tar (Rozhan & Purwanto, 2015). Flash pyrolysis produces high volumes of liquid (bio oils). On the other hands, slow heating pyrolysis generates high yield of char (Wang et al., 2016). During the carbonization process, moisture content was reduced to residual values below 3.6%. This moisture reduction is essential to improve the combustion efficiency. However, thermal decompositions

cause structure rearrangement, which decreases the number of hydroxyl groups in the biochar surface that becomes more hydrophobic. In the carbonization process, the temperature attacks the organic matter that causes cracking, surface changes, rearrangement of dimension, decline in volume due to shrinkage and mass loss (Sebbahi et al., 2014). Pyrolysis temperature is the serious parameter in pyrolysis followed by heating rate, inert gas flow rate and the holding time.

2.8.2 Activation Step

The carbon can be activated by two methods. Such as physical processes and chemical activations. Commercial activated carbons are produced widely with these processes (Alslaibi et al., 2013). To prepare promising activated carbon is used a physicochemical activation method (Yahya et al., 2015). Activation step is used to improve the porosity of char by increasing the pore diameter and developing new pores (Alslaibi et al., 2013).

2.8.2.1 Physical Activation

Generally, in the physical activation process, originator bio char can be converted into activated carbon through two step methods. The first step is carbonized of the precursor by pyrolysis at (400 to 1000 °C) under nitrogen gas flows (Adegoke & Bello, 2015). It follows some activation factor which involves the contact of the char with steam, oxidizing gas (CO_2), and air without the presence of a catalyst (Alslaibi et al., 2013). During the process, carbon atom rearrangement occurs into graphite-like structure (Yahya et al., 2015). Aromatic structure creates a rigid carbon frame. It happens due to the elimination of non-carbon elements from polymeric cellulose or lignin. The second stage is the broadening of the existing pores of larger-sized pores. Carbon dioxide (CO_2) is usually used as an activating gas in the physical activation process. It is a clean gas which is easy to handle and is capable of assisting control of the activation process. Because, the reaction rate is slow at 800 °C. Activated carbons

produced by the physical activation process lack satisfactory characteristics as adsorbents (Adegoke & Bello, 2015).

Ahmad et al. (2013) suggested that the significant effect of the physical activation method was to produce porous structures of activated carbons using CO_2 on cocoa shell waste. It observed that the char was highly microporous with a narrow pore size distribution at temperature below 600 °C. At 600 °C, produced char showed higher uptake of CO_2 compared with char carbonized at 400 and 500 °C. At temperature above 600 °C, it was found to decrease in CO_2 uptake, an indication of low surface area. Guo et al. (2009) observed similar findings that while with increasing activation temperature from 700 to 900 °C, the yield and average pore diameter of the prepared activated carbons decreased; the surface area and pore volume increased. This happens due to a combination of liberating the volatiles from the char and char oxidation with carbon dioxide. Varies activating temperature is needed to produce activated carbon from natural waste. Sometime are using high temperatures (800 °C) while others experimenting with low temperatures (300 to 500 °C). The optimum condition to produce activated carbon depends on the raw material itself. Selection of activation temperature and activation agent use is also important (Aworn et al., 2008). Table 2.1 shows previous studies on production of activated carbon using the physical activation process.

Table 2.1 A list of some activated carbon produced from agricultural waste using physical activation method

Raw Material	Activating Agent	Activation Temperature (°C)	Reference
Coconut shell	CO_2	900	(Rashidi et al., 2014)
Palm shell	Steam	900	(Guo & Deng, 2013)
Bean pods	Steam	700	(Cabal et al., 2009)
Macadamia nut-shell	Steam	800	(Aworn et al., 2008)

2.8.2.2 Chemical Activation

Generally, in the chemical activation process, carbonization and activation steps occur concurrently with the aid of chemical activating agents during the impregnation

process (Yahya et al., 2015). Activating agents such as zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4) (Suhas et al., 2007; Chen et al., 2011) sodium carbonate (Na_2CO_3), sulphuric acid (H_2SO_4) (Karagöz et al., 2008), and potassium carbonate (K_2CO_3) (Chen et al., 2011) are commonly used to produce activated carbon by chemical activation. These agents can inhibit tar improvement and decrease the volatile matter growth of impregnated precursors (Chandra et al., 2009). During chemical activation methods, more than one chemical (activating agent/s) can be applied in a single production. The activating agents support the improvement of the carbon porosity through dehydration (Kumar & Jena, 2016) and degradation mechanisms (Ioannidou & Zabaniotou, 2007). Chemical activation generally carries out at such type of temperature: 300 to 700 °C, 400 to 700 °C, 400 to 800 °C or 500 to 800 °C. (Yahya et al., 2015) suggested that chemical activation is one kind of wet oxidation which requires impregnation of activating agent into the precursor. Activated carbon is the end-product after washing procedure.

This type of activation acquires its name from the usage of inorganic additives (activating agents) which play a vital role in degrading and dehydrating the cellulosic materials in the precursor (Yahya et al., 2015). Activating agents inhibit the formation of the ash (Yahya et al., 2015), improve porosity and increase the carbon yield (Rodriguez-Reinoso & Molina-Sabio, 1992). According to (Chen et al., 2011), chemical activation has been done at 400 to 900 °C. The contact between the activating agents and the carbon structure permits the application of a lower temperature compared with that of physical activation. On the other hand, prior to applying the prepared activated carbon, the residual chemicals need to be detached from the carbon using distilled water (Alslaibi et al., 2013). There are some main advantages of chemical activation in comparison to physical activation as listed below:

i. The activation needs a lower activation temperature, therefore can reduce the cost of energy.

ii. The chemical activation created higher carbon yield than the physical activation (Acharya et al., 2009).

iii. It needed less activation time (Alslaibi et al., 2013).

iv. It can improve high porosity carbon structure (Alslaibi et al., 2013).

Chemical activation has the capability to suppress the tar or ash production which results in high carbon yield (Purnomo et al., 2012). Besides, a development of oxygenated groups on the activated carbon can be improved by chemical activation (Gad & El-Sayed, 2009). The chemical activation process is more useful, where the produced activated carbon is furnished with higher porosity and better surface area (Ioannidou & Zabaniotou, 2007). Activating agents have a great effect on the pore enlargement and surface characteristics (Sahira et al., 2013). Table 2.2 showed a summary on application of chemical activation method in preparation of activated carbons using agricultural waste as precursor.

Table 2.2 A list of some agricultural activated carbon prepared using chemical activation technique

Raw Material	Activating Agent	Activation Temperature (° C)	Reference
Palm oil shells	Na_2CO_3, $ZnCl_2$,	700	(Hussaro & Rattanakosin, 2014)
Corn cobs	H_3PO_4	500	(Njoku & Hameed, 2011)
***Jatropha curcas* shell**	NaOH	700	(Tongpoothorn et al., 2011)
Bamboo	H_3PO_4	200 (microwave)	(Liu et al., 2010)
Sugar beet bagasse	$ZnCl_2$	500-700	(Demiral & Gündüzoğlu, 2010)
Soybean oil cake	K_2CO_3, KOH	600 – 800	(Tay et al., 2009)

2.8.2.3 Physico-chemical Activation

The combination of chemical and physical activation processes is called physicochemical activation. Physicochemical activation is highly desirable where high quality activated carbon with larger surface area can be produced. But this type of

activation is costly (Mohd Din et al., 2009). Physicochemical activation is carried out by concurrently activating the precursor with physical and chemical activation. This type of process is generally carried out at high temperature (600 to 850 °C) in the presence of activating agent (e.g. K_2CO_3, $ZnCl_2$, H_2SO_4 or H_3PO_4) under the flow of oxidizing agent such as CO_2 or steam (Salman & Hameed 2010). (Nowicki et al., 2015), succeed to produce microporous activated carbons with surface areas ranges of 361 to 1173 m^2/g from cherry stones. According to (Huang et al., 2015), that application of CO_2 in activation technique was effective in increasing the surface area and the formation of mesopores in the activated carbon. (Veksha et al., 2016) observed that the effect of interaction between KOH and CO_2 or steam gasification in pore opening can well developed pore structure.

Table 2.3 A list of some application of physic-chemical activation technique in preparation of activated carbon

Raw Material	Activating Agent	Activation Temperature (°C)	Reference
Aspen wood	KOH/CO_2	900	(Veksha et al., 2016)
Olive stones	KOH/CO_2	800	(Temdrara et al., 2015)
Giant-knotweed	KOH/CO_2	800	(Fałtynowicz et al., 2015)
Cherry stones	KOH/CO_2	800	(Nowicki et al., 2015)
Oil palm fronds	KOH/CO_2	850	(Salman & Hameed, 2010)
Coconut shell	KOH/CO_2	850	(Mohd Din et al., 2009)

2.8.3 Ash in Activated Carbon

The development of highly mesoporous structure can be produced by using acid treatment with temperature. Acid treatment reformed the surface chemistry by discharging the acidic and phenol groups linked to calcium. Ash is a troublesome compound in activated carbon. It can interrupt the porousness (Ahiduzzaman & Sadrul Islam, 2016). It is present as an impurity form when the carbonaceous material is burned off. There are some inorganic such as silica, and other metal oxides such as calcium oxide (CaO), magnesium oxide (MgO) and potassium oxide (K_2O) present in the organic material. These are usually formed from the ash content (Danewalia et al.,

2016). However, ash can be removed from the activated carbon using acid or alkali solutions (Ahiduzzaman & Sadrul Islam, 2016). According to Ahmad et al., (2013), cocoa activated carbon had proved an increase in surface area from 367 m^2/g to 1,000 m^2/g after acid treatment.

2.9 Characterization of Activated Carbon

The performance of an activated carbon depends on its characteristics and properties. Qualitative and quantitative information of activated carbons can provide a foundation for assessment and assortment of activated carbons for applications. This evidence is also beneficial for modelling the characteristics and performance of activated carbons. The functional groups of activated carbon are determined using FTIR spectroscopy technique. The common measured data are surface area, average pore size, pore size distribution, pore volume, and the surface chemistry of the carbon. The most popular method to measure surface area and porosimeter of activated carbons is by using BET model equation and pore volume using BJH model. Microscopic methods are another method to show the micro and sub micro aspects of activated carbons by using Scanning Electron Microscopy (SEM) (Achaw, 2012).

2.9.1 Physical Properties

Physical properties of activated carbons are a very essential factor of the adsorption process. The types of their structures (macropore, mesopore or micropore) set them with their adsorption manner and describe their porosity. Surface area and pore size are very important elements in liquid adsorption. On the other hand, pore volume is also a vital component, where the ratio between the pore structure and the pore volume can be useful in the adsorption capacity methods.

2.9.1.1 Carbon Yield

There are some important parameters like the carbonization time, temperature and the flow rate of carbon dioxide (CO_2) or steam in physical activation to optimize the preparation of the activated carbon. The impregnation duration and ratio of activation process are also important. The characteristics of the prepared activated carbons can be affected by the raw material and the activation method effect (Tan et.al., 2008). Both activation methods affect the carbon yield. Physical activation method produces activated carbon with lower carbon. The type of pore structure is usually microporous. Chemical activation systems produce higher carbon material than physical activation methods. Generally, raw materials with high content of volatiles are treated with chemical activation methods to produce the activated carbon. Yield (in percentage) of activated carbon is established from the calculation of ratio of the dry weight (g) of the prepared activated carbon, w_c to the dry weight (g) of the precursor, w_o as shown in Equation 2.1 (Wu et al., 2013).

$$\text{Yield (\%)} = \frac{Wc\ 100}{Wo} \qquad (2.1)$$

Where, w_c is the dry weight (g) of after activation product and w_o is the dry weight (g) of the precursor. This quantity was measured to study the efficiency of the activation process (Ahmad et. al., 2011).

Usually, with the increase in pyrolysis temperature would decrease the yield of char. As the temperature is raised, the ash and fixed carbon contents are also higher but the volatile matter is decreased (Zhao et al., 2017). During carbonization, at higher temperatures (600 - 700 °C) can increase the release of liquid and gases. But at the same time, decrease the char yield. At high temperatures, this occurs due to the effect of the primary decomposition of precursor and the secondary decomposition of char. As a result, high carbonization temperatures run a higher quality char but lower the yield (Zhao et al., 2017). The secondary decomposition of the char converts into non-condensable gaseous products that adds to the increase in gas yield (Mazlan et al., 2015). Yahya et al. (2015) suggested that agricultural waste and lignocellulosic material can yield lower activated carbons than hard raw materials such as coal and peat. But

these materials can produce a higher-quality activated carbon which is the top concern. Activated carbon with highly porous structures can be produced by reducing volatile matters from the raw materials (Yahya et al., 2015).

2.9.1.2 Activated Carbon Structure

There are some forms of activated carbon like crystallites, graphitic layers, and stacks of horizontal planes due to carbonization (Mopoung, 2008). Activated carbon is an internally well-developed pore structure. Generally, the developed pore structure describes the surface area and porosity of the adsorbents. It can be divided into micro, meso and macropores (Bhatnagar et al., 2013). Much concentrate was given to the effect of pyrolysis pressure to form the chars and liberation of ash. Such effects can be observed by the incidence of plastic deformation where particles were melted at high heating rates. This phenomenon generally correlates with carbon species which contain volatile matter (Tchapda & Pisupati, 2014).

2.9.1.3 Pore and Surface Area Characteristics

The main properties of an activated carbon are surface area, pore volume and pore size distributions. There are some important factors during produced activated carbon such as activation temperature, activation time and chemical impregnation ratio. It will affect the development of pore and surface profiles of the adsorbent (Guo et al., 2009). Pore size distribution and porosity of activated carbon characterize its pore space that portion of the carbon's volume which is not engaged by solid material (Nimmo, 2004). A pore is a hole or cavity on the outer surface of an adsorbent. It has a large effect on the performance of an activated carbon. The pore space is usually measured in terms of individual pores. Porosity is the ratio of voids to solids in an activated carbon. It is the fraction of the total volume that is taken up by the pore space (Nimmo, 2004). Pore size distribution is a very important asset of adsorbents. It describes the fraction of the total pore volume accessible to molecules of a given size and shape. According to IUPAC,

the pores of absorbents can be divided as a group into micropore, mesopore and macropore.

2.9.1.4 Surface Morphology

The surface morphology of adsorbents can be described by Scanning Electron Microscope (SEM) (Yakout & Sharaf El-Deen, 2016). Sometime can use another process like Transmission Electron Microscope (TEM). In common practice, the pore structure, surface structure and pore arrangement of activated carbon is shown through SEM. SEM is appropriate due to its ability to verify the presence of porosity and pore development (Ahmad & Alrozi, 2010).

2.9.2 Chemical Properties

Chemical characterisation of an activated carbon is signified by proximate analysis and surface functional groups.

2.9.2.1 Proximate Analysis

Proximate analysis is carried out to determine the moisture, ash and volatiles matter content due to evaluate the fixed carbon of adsorbents. Elemental analysis is performed to calculate the percentage of carbon, hydrogen, nitrogen, oxygen, and sulphur present in a precursor (Wu et al., 2013). During the production of activated carbon, high temperature can remove the moisture, some ashes and the volatile matter contents of the precursor to produce solid char and activated carbon. This leads to shell-based activated carbon. Development of porous structure, larger surface area, variation in pore structures (Ioannidou & Zabaniotou, 2007). The inorganic material contained in activated carbon is measured as ash content.

Most lignocellulosic materials are composed mainly of oxygen, carbon, and hydrogen. From the study of peanut shell material observed that there was 48 % of oxygen, 45 % of carbon and 6 % of hydrogen. It was also proven that the ash content may be due to the presence of potassium, calcium, silicon, and sodium. Mineral contents contained in the precursor could encourage various reactions engaged in the production of activated carbon and could enhance for higher reactivity which support the process (Wu et al., 2013).

2.9.2.2 Surface Functional Groups

Produced adsorbents are formed by some surface functional groups. Generally, it relied on the precursor and method of activation (Suhas et al., 2007). Kalijadis et al. (2011) had stated that Boehm method can be applied to determine the surface oxygen groups on an activated carbon with acidic and basic properties. The O-containing groups are the most essential surface functional group which provides features such as polarity, hydrophilic and acidic character (Li, 2012). Allwar (2012) suggested that the activated carbons have oxygen functional groups consisting of carboxylic, phenol or lactonic groups besides aromatic hydrocarbons ring. Acid such as sulphuric acid, nitric acid can modify the surface functional groups of activated carbon by increasing the presence of acid groups. This may be occured due to the removal of inorganic compounds and the left sites on the carbon were filled with oxygen by chemisorb. Additionally, the increase in intensity of C=O, O-H and C-O (phenol group) in the FTIR spectra show the available oxygen functional groups on the activated carbon.

2.10 Adsorption Factors

At the equilibrium time, adsorbents show the maximum adsorption capacity (Azouaou et al., 2010). The Absorption process depends on some important factors. The pH of the solution was an essential factor for adsorption methods (Azouaou et al., 2010); (Babu & Gupta, 2008). The influence of pH relied on the charge of adsorbent. Adsorption capacity depends on differences between initial and final concentration of

metal ions. These concentrations were measured by Atomic Absorption Spectroscopy (AAS). Adsorption ability is evaluated by this data (Azouaou et al., 2010). Adsorption process also relies on dosage of the adsorbent which is an important factor due to calculating the adsorbent ability. The reduction of heavy metals increases with dosage. The binding ability was considered by using the different amount of adsorbents (Azouaou et al., 2010).

2.11 Adsorption Equilibrium Models

Adsorption isotherms are probably the best techniques to calculate the amount of adsorbate from solution. It can retain and remain in the solution after equilibrium. This also provides the design of adsorption systems. It expresses the external properties and attraction of the adsorbent for different pollutants. They can also be used to relate the adsorptive capabilities of the adsorbent for varieties of pollutants.

2.11.1 Langmuir Isotherm

The Langmuir isotherm suggests that it is valid for monolayer adsorption at specific homogeneous sites on the adsorbent surface. Generally, once the adsorbate is involved on the identical site. Consequently, no more adsorption can take place at that same site. It's settled that the adsorption process is monolayer in nature (Mohd Din et al., 2009). The isotherm points out that monolayer adsorption may happen on the surface of the adsorbent formed with homogeneous adsorption patches (Ng et al., 2017).

The Langmuir equation is founded on assumptions as stated by (Desta, 2013):

i) Monolayer adsorption onto a surface containing a specific adsorption site.

ii) No shifting of adsorbate in the smooth surface.

iii) Sorption stops when the adsorption site is occupied.

The Langmuir isotherm equation is given by the below equation (Babu and Gupta, 2008):

$$q_e = \frac{q_{max}\ b\ Ce}{1+b\ Ce} \quad (2.2)$$

The linear form of Langmuir isotherm equation is stated by Equation 2.3

$$\frac{Ce}{qe} = \frac{1}{qmax\ b} + \frac{Ce}{qmax} \quad (2.3)$$

Where, C_e is the equilibrium concentration of the solute (mg/L), and C_o is the initial concentration of adsorbate. Other hand, q_e is the amount of solute bind per unit mass of adsorbent (mg/g), q_{max} is the maximum monolayer binding ability of the adsorbent (mg/g). Even, b is the Langmuir adsorption constant related to the free energy adsorption (L/mg). The constant value can be calculated from the linear plot. That is investigational data of (Ce/qe) versus Ce.

The Langmuir equation can be stated in terms of dimensionless separation factor, R_L, defined as (Dada, 2012):

$$R_L = \frac{1}{1+b\ Co} \quad (2.4)$$

where, R_L value indicates the adsorption to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

2.11.2 Freundlich Isotherm

The Freundlich isotherm suggests that adsorption happens on a surface of adsorbent through a multilayer adsorption mechanism (Kalavathy et al., 2005). This isotherm is applied for heterogeneous exterior substances in which active sites are not identical.

The adsorption intensity of the adsorbent is considered by this isotherm. The isotherm model is stated by below equation (2.5) (Dada, 2012):

$$q_e = K_f C_e^{1/n} \quad (2.5)$$

where q_e is the amount of solute bound at equilibrium, (mg/g), and C_e is the equilibrium concentration of adsorbate, (mg/L). Besides, K_f is the Freundlich constant, (mg/g) (L/mg) 1/n and n is the Freundlich heterogeneity factor. The equation is conveniently used in the linear form by taking the logarithm of both sides as equation (Dada, 2012):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2.6)$$

A plot of (log q_e) against (log C_e) a straight line shows the confirmation of the Freundlich isotherm. Here, the constant value can be gained from the slope and intercept of the linear plot. Where, the value of n indicates favourable adsorption when $1 < n < 10$.

2.11.3 Dubinin – Radushkevich (D-R) isotherm

Physical and chemical properties can not be clearly described by the Langmuir and Freundlich model. This problem can be solved by Dubinin – Radushkevich (D-R) isotherm model. Since, the mean adsorption energy (E) can describe this. It is obtained from the D-R model. This model is used to define the adsorption isotherms of single solute systems (Azouaou et al., 2010; Elangovan et al., 2008). The D-R isotherm is expressed as:

$$q = q_{max} \exp\left(-B \left[RT \ln\left(1 + \frac{1}{Cf}\right)\right]^2\right) \quad (2.7)$$

$$\ln q = \ln q_{max} - B e^2 \quad (2.8)$$

where B is the adsorption energy constant, R is the gas constant (8.314×10^{-3} kJ/molK) and T is the absolute temperature.

(2.9) $e = RT \ln (1+\frac{1}{Cf})$

(2.10) $E = 1/(2B)^{0.5}$

Adsorption properties can be described by this parameter of the mean adsorption energy (*E*). When the value of *E* is between 8 and 16 kJmol^{-1}, it can follow chemical adsorption. On the other hand, the values of *E* are below 8 kJmol^{-1}, it follows physical adsorption.

2.12 Adsorption Kinetics Models

The adsorption kinetics shows the rate of adsorbate adsorb on adsorbent which controls the equilibrium time. Due to select the optimum conditions for adsorption, the adsorption kinetics is important. The kinetic parameters are important to predict the adsorption rate. These parameters are: the effects of initial concentration, contact time, pH and adsorbent dosage (Kalavathy et al., 2005). In fact, kinetic models are valuable in determine the significance of diffusion mechanisms inside the adsorbent particles (Demirbas, 2008). Such kinetic models for liquid-phase adsorption are pseudo first - order, pseudo second-order models and intra particle diffusion models (Kalavathy et al., 2005). The adsorption techniques will be affected by the physical and chemical characteristics of the adsorbent (Ruíz-Baltazar & Pérez, 2015). The kinetic data may be well-fitted to either the pseudo-first or second order kinetic models (Theivarasu & Mylsamy, 2010).

2.12.1. Pseudo-First-Order Kinetic Model

This model has been broadly used for the prediction of adsorption kinetics (Srihari & Das, 2008). The model is described as in equation 2.11:

(2.11) $\frac{dqt}{dt} = k_1 (q_e - q_t)$

Here, q_e is the amount of solute adsorbed at equilibrium, (mg/g), q_t is the amount of solute bind with adsorbent at time, (mg/g). Where k_1 is the rate constant of pseudo-first order sorption (1/h). Integrating equation 2.11 for the boundary conditions t =0 to t and q_t =0 to q_t, gives the following equation:

$$log\ (q_e - q_t) = log\ q_e - \frac{k1\ t}{2.303} \quad (2.12)$$

Removal of the logarithm constant as in equation 2.13, below.

$$ln\ (q_e - q_t) = ln\ q_e - k_1\ t \quad (2.13)$$

The graph of ln ($q_e - q_t$) Vs t provides a slope of k_1 and an intercept of ln q_e.

2.12.2. Pseudo-Second-Order Kinetic Model

On the other hand, the pseudo second-order model predicts the performance over the whole range of adsorption. It is an adsorption mechanism being the rate controlling step (Bulut et al., 2008). At equilibrium, the pseudo-second-order equations can be expressed as equation 2.14:

$$\frac{dqt}{dt} = k_2\ (q_e - q_t)^2 \quad (2.14)$$

Here, q_e is the amount of solute adsorbed at equilibrium, (mg/g), q_t is the amount of solute bind of adsorbent at time, (mg/g). Where, k_2 is the rate constant of pseudo-second-order sorption (g/h.mg). Then Integrating equation 2.14 for the boundary conditions t = 0 to t and q_t = 0 to q_t, provides the below equation:

$$\frac{1}{qe - qt} = \frac{1}{qe} + k_2\ t \quad (2.15)$$

That is the integrated rate low for a pseudo-second-order reaction. Here, Equation 2.15 can be rearranged to gain linear form:

$$\frac{t}{qt} = 1/\ k_2\ q_e^2 + \frac{t}{qe} \quad (2.16)$$

The linear graph of t/q_e Vs t provides $1/q_e$ the slope and $1/k^2q_e^2$ as the intercept.

2.12.3 Intra-Particle Diffusion

The adsorption and kinetic isotherm can be used for describing techniques of the adsorption process. This is to characterize the adsorption process, whether it is boundary layer diffusion or intra-particle diffusion or both (Klaewkla, 2011). The effect of intra-particle diffusion can be determined by the equation 2.17:

$$q_t = K_{id}\, t^{1/2} + C_i \qquad (2.17)$$

where K_{id} is the intra-particle diffusion rate constant (mg/g $min^{1/2}$). From Equation 2.17 shows a plot of q_t against $t^{1/2}$, derived to give a linear plot with slope K_{id} and intercept C_i. The C_i value is used as a thickness of the boundary layer where the larger the value, the greater the contribution of the surface sorption in the rate-controlling step. A different nature of the plotted graphs can be shown due to the wavering of sorption at the initial stage and at the final stage of the adsorptions. This phenomenon can be due to boundary layer diffusion which occurred at the initial stage and the intraparticle diffusion which occurred in the later stage (Kumar et al., 2011). The linear regression of the plot that passes through the origin indicates an intraparticle diffusion as its rate-limiting step. The linear plots that fail to pass through the origin are assumed to be due to the difference in the rate of mass transfer in the initial and final stages of adsorption (Kumar et al., 2011).

2.13 Adsorption Mechanism of Activated Carbon

The different techniques to adsorb pollutants onto AC are exposed in Figure 2.6:

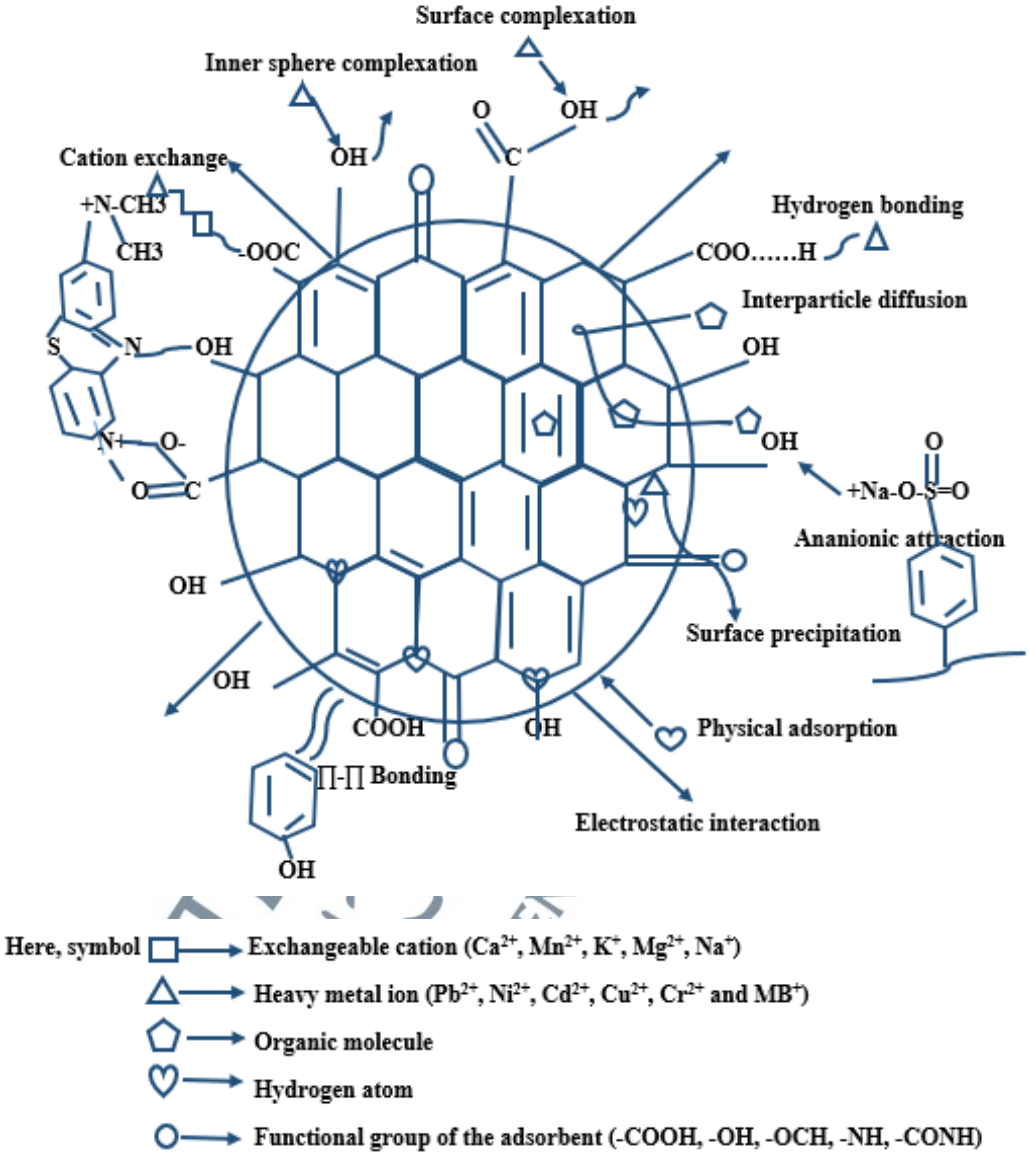

Figure 2.6 Adsorption mechanism of different types of the pollutants

There are many different mechanisms for activated carbon adsorption such as Van der Waals forces, electrostatic interactions, ion exchange mechanisms, pie-pie interactions, hydrogen bond formation, diffusion process, precipitation and so on (Alam et al., 2020). Adsorption can be occurred onto the adsorbent surfaces like varieties of organics, inorganics, heavy metals, surfactants, dyes and so on. The adsorption mechanism on adsorbent to remove pollutants follows four varieties steps such as (1) adsorbate come to the surface of the adsorbent, (2) formed film diffusion onto the outer surface of adsorbent, (3) adsorbate diffusion internal side of the pore and (4) contact between adsorbate and adsorbent pores. The control of the final step are very tough and with each other interaction might be strong or weak (Ahmed et al., 2015 & Sarkar et al., 2003). The whole adsorption process has an important factor which is rate limiting factor (Sarkar et al., 2003). If the adsorbate and adsorbent come to contact with each other and opposite charge contains then it can exchange cation and anion by ion exchange method. Here, in ionic compounds, electro-kinetics potential, that is zeta potential, plays an important role for the adsorption process of adsorbents. According to the four step mechanism, the adsorbents of activated carbon adsorb methylene blue from wastewater by forming of MB^{+} cation (Kannan & Meenakshisundaram, 2002). The surface of adsorbents which have oxygen contain functional groups like (-COOH, -OH) can show strong effects on the adsorption to remove pollutants especially heavy metals ion (Zn^{2+}, Ni^{2+}) (Kannan & Meenakshisundaram, 2002). Other side's soft metal ion (Pb^{2+}) can be adsorbed by the pie (π) electrons of the adsorbent surface (Alfarra et al., 2004 & Badruddoza et al., 2013). Activated carbon can participate in hydrogen bond formation with organic contaminants where at least one hydrogen atom presents inside of adsorbate and adsorbent molecules (Considine et al., 2001 & Ahmed et al., 2018). Activated carbon involves varieties π–π interactions with adsorbate. Basically, this type of interaction is a non-covalent interaction where at least one pie π- electron rich group is needed, like an aromatic ring. It can help with crystal structure formation, chemical bonding, boiling points and solvation energies etc. Depending on the functional group on the adsorbents and pH of the solution, it can act as an electron donor or acceptor site. There are three types of interaction between adsorbate and adsorbents such as electron–donor-acceptor interactions, electron–acceptor-acceptor interaction and electron-donor-donor interaction. Here electrons –donor-donor-interaction are the best interaction than

others. Generally, this type of interaction can control the adsorption mechanism of activated carbon (Ahmed et al., 2018). At last, there are some other weak bonds like Van der Waals forces, surface deposition and non-defined covalent bonds.

2.14. Regeneration and Desorption of Used AC

2.14.1. Regeneration

Regeneration is a very important factor of activated carbon for highest profit. After using adsorbent, it is needed to check reusability and explain the adsorption technique for reusing it more and more time due to reduced cost of process (Nikman et al., 2017). Regeneration process can be completed using some process such as solvent extraction (Lu et al., 2011), oxidizing (Cabrera-Codony et al., 2015), thermal (Li et al., 2018) and biological regeneration. For the desorption of organic compounds from adsorbents, the solvent extraction method is the most usable process. Some usable solvent are ethanol, chloroform, acetone, benzene and so on (Lu et al., 2011). Oxidation method also can be used for the regeneration of activated carbon using hydrogen peroxide (H_2O_2) and ozone (O_3) (Anfruns et al., 2013). It is need to explain the mechanism of adsorption.

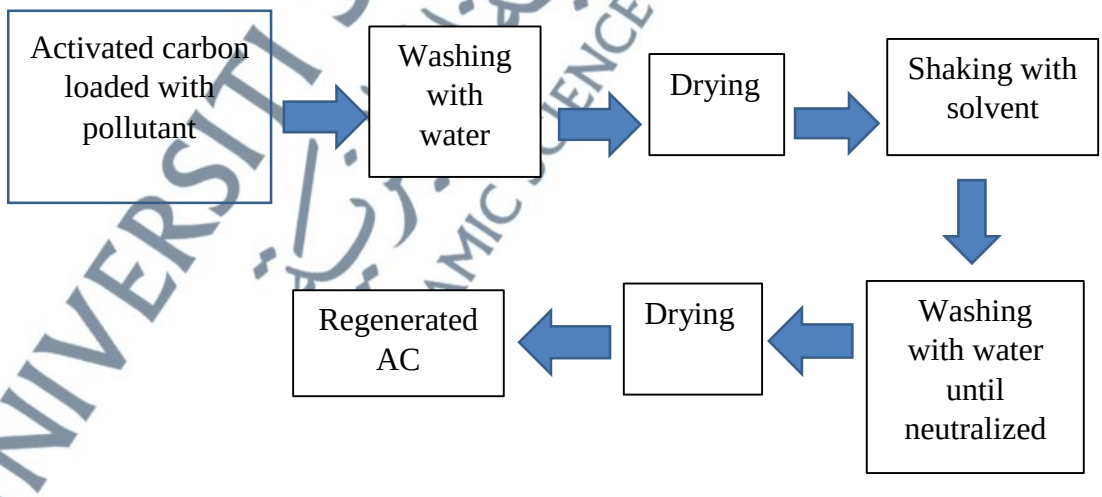

Figure 2.7 Regeneration process of activated carbon

Other hand, the thermal regeneration process has advantages and disadvantages. Main drawbacks of the thermal process are formation of non-volatile compounds on the surface and increase the weight loss of activated carbon (Cabrera-Codony et al., 2015; Li et al., 2018). Micro-organism can be used to regenerate adsorbents and stability is high after regeneration.

2.14.2. Desorption of Organics and Heavy Metals

Desorption process of activated carbon is required for future reusing and recovery of adsorbent and adsorbate. There are some important factors for a well desorption process like the quantity to be adsorbed, cost consideration and method requirements. This type of desorption process needs a shaker for shaking. There are several solvents for the desorption process such as HCl, H_2SO_4, HNO_3, and Na_2CO_3. Hydrochloric acid (0.1N) is the most used solvents to desorb contaminants from adsorbent (Bello et al., 2010). Organic solvents like ethanol, methanol, ether and aldehyde can be used to desorp on organic pollutants from activated carbon. Benzene and toluene are desorbed from adsorbents which are dependent on solubility and chemical structure. There are some metals such as Cr (VI) and Ni (II) that are desorbed from adsorbent by applying Na_2CO_3. Chelating agents like EDTA are shown to have a good capability to desorb pollutants from adsorbents (Akhtar et al., 2010).

Activated carbon can be converted into alternative materials (like syngas) through thermal process (gasification). Organic compounds contaminated adsorbents can be used for producing syngas. On the other hand, heavy metals loaded with activated carbon can be used in soil. Firstly, heavy metals are desorbed from HM loaded activated carbon then it is applied to soil. Additionally, the regenerated activated carbon (fly ash) can be applied as a part of a cement composite. Activated carbon also can be used in building construction as a biochar. Finally, it can be used more and more in the adsorption-desorption process.