PHYSICOCHEMICAL CHARACTERIZATION FOR DIFFERENT TYPES OF SOIL USED IN HEAVY METALS REMOVAL FROM AQUEOUS SOLUTION

MOHD SYUKRI BIN RAMLI

SCHOOL OF HEALTH SCIENCES
UNIVERSITI SAINS MALAYSIA

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PHYSICOCHEMICAL CHARACTERIZATION FOR DIFFERENT TYPES OF SOIL USED IN HEAVY METALS REMOVAL FROM AQUEOUS SOLUTION

by

MOHD SYUKRI BIN RAMLI

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CERTIFICATE

This is to certify that the dissertation "**Physicochemical Characterization for Different Types of Soil Used in Heavy Metals Removal from Aqueous Solution"** is the bona fide record of research work done by MOHD SYUKRI BIN RAMLI, matric number P-SKM0052/19 from February 2020 to September 2020 under my supervision. I have read this dissertation and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation to be submitted in partial fulfilment for the degree of Master of Science (Forensic Science). Research work and collection of data belong to the Universiti Sains Malaysia.

Main supervisor

…………………………………………..

Dr. Nurasmat binti Mohd Shukri

Lecturer

School of Health Sciences

Universiti Sains Malaysia

Health Campus

16150 Kubang Kerian

Kelantan, Malaysia

Date: 10/09/2020 ……………………………………

DECLARATION

I with this declared the dissertation is the results of my investigation, except where otherwise stated and duly acknowledged. I also claim that it has not previously or concurrently submitted as a whole for any other degrees at Universiti Sains Malaysia or other institutions. I grant Universiti Sains Malaysia the right to use the dissertation for teaching, research and promotional purposes.

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Mohd Syukri bin Ramli

10/09/2020

Date: ………………………………………..

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LIST OF ABBREVIATIONS

>	Higher than
%	Percentage
As	Arsenic
BET	Brunauer, Emmet and Teller
Cd	Cadmium
Cr	Chromium
Cu	Copper
EDX	Energy Dispersive Xray
Fe_2O_3	Metal Oxide
FESEM	Field Emission Scanning Electron Microscope
Fe	Metal
FTIR	Fourier Transform Infrared
Hg	Mercury
Si	Silica
Pb	Lead
Zn	Zinc

PENCIRIAN FIZIKOKIMIA BAGI TIGA JENIS TANAH YANG DIGUNAKAN DALAM PENYINGKIRAN LOGAM BERAT DARIPADA LARUTAN AKUEUS

ABSTRAK

Logam berat merupakan salah satu punca pencemaran air dunia. Kajian penjerapan menggunakan tanah dikenalpasti sebagai satu langkah terbaik untuk nyahcemar logam berat dari perairan. Kajian sebelumnya mendapati tiga jenis tanah berjaya menjerap sejumlah logam berat seperti merkuri, dan juga cadmium dari larutan. Maka, kajian ini dijalankan untuk mendapatkan karakterisitk fisikokimia terhadap tiga jenis (tanah merah, berpasir dan tanah liat) yang merupakan penjerap untuk nyahcemar bahan logam berat di dalam sumber air kita. Kesemua jenis tanah tersebut dianalisa menggunakan instrumen *Field Emission Scanning Electron Microscope-Energy Dispersion X-ray* (FESEM-EDX), *Fourier Transform Infra-Red* (FTIR) dan*Brunauer, Emmett and Teller* (BET). FESEM akan menghasilkan imej struktur untuk jenii tanah tersebut. Peratusan tertinggi untuk jumlah besi (Fe) adaalah tanah berpasir (10.72%) diikuti tanah liat (4.38%) dan tanah merah (3.87%), yang dikesan menggunakan EDX. Ini membuktikan bahawa sampel tanah dengan kehadiran Fe membantu nyahcemar logam berat itu. Kehadiran silika, hidroksil dan juga karboksil pada semua jenis tanah disahkan dengan menggunakan instrumen FTIR. Analisa BET pula mendapati saiz liang tanah berpasir dan liat lebih kecil dari tanah merah. Saiz liang kecil memiliki jumlah permukaan yang luas dan menjayakan proses penjerapan bahan logam berat ini. Hanya tanah berpasir sahaja mempunyai pengiraan jumlah luas permukaan dengan analisa BET. Keputusan kajian ini merupakan perestujuan yang memeberi kesimpulan bahawa karakter fisikal tanah berpasir meningkatkan kadar penjerapan logam berat berbanding tanah merah dan tanah liat.

PHYSICOCHEMICAL CHARACTERIZATION FOR DIFFERENT TYPES OF SOIL USED IN HEAVY METALS REMOVAL FROM AQUEOUS SOLUTION

ABSTRACT

Heavy metals are one of the main contributors to water pollution worldwide. The adsorption study using soil known to be a promising technique to remove heavy metals from aqueous solution. The previous study claimed that these three types of soil (red-earth, clay and sandy soil) have successfully adsorbed considerable quantities of heavy metals such as lead (Pb) and cadmium (Cd) ions from aqueous solution. Thus, this study intended to examine the physicochemical characteristics of three types of soils (red-earth, clay and sandy) which acted as adsorbents material to remove the heavy metals from aqueous solution. All soil sample types were characterized and analyzed using Field Emission Scanning Electron Microscope-Energy Dispersion X-ray (FESEM-EDX), Fourier Transform Infra-Red (FTIR) and Brunauer, Emmett and Teller (BET). FESEM micrographs demonstrated different structural images of all soil samples. The highest percentage amount of metal (Fe) was sandy soil (10.72%) followed by clay soil (4.38%), and red earth soil (3.87%) was detected using EDX analysis. These proved that all the samples have Fe metal that facilitates the removal of heavy metals. FTIR spectra confirmed the presence of silica, hydroxyl and carboxyl functional groups in all types of soil. The BET data revealed that the pore size of sandy and clay were smaller than red-earth soil. A smaller pore size serves a larger surface area that leads to a successful adsorption study. The only surface area of sandy soil could be calculated using the BET analysis. The finding of this study is in mutual agreement with the previous research which concluded that the physical features of sandy soil yielded a higher percentage of heavy metal removal compared to red-earth and clay soil.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water is an essential element for living life. As the earth's surface is covered with over two-third with the water, we must safeguard our water supplies, for the next generation. Water supplies are varied, including oceans, rivers, lakes and groundwater, which is used in our daily routine, as in domestic usage, commercial and for the agriculture activities. The usage of water has been increased globally six times after a decade, and the rate will dramatically increase one per cent every year due to larger population, development of economic activities, and changes in consumption trends (UNESCO, 2020).

Unfortunately, those human activities give a severe threat to the water supplies with a risk of water pollution. The emerging water pollution problems lead to many issues, such as lack of fresh water supplies, increasing the amounts of wastewater that will jeopardize human's health. Water pollution happens when any harmful substances, which includes chemicals or any microorganism presence in our water supplies, and contaminates which will lead to the degradation of water quantity and toxic to the environment and human being. Example of freshwater pollutants is organic waste, pathogens, fertilizers, pesticides, and heavy metals that heavily used in human activities.

Heavy metals are a category of the group of metals and semimetals elements that have a high risk of pollution and possible toxicity especially, towards human health. It is one of the industrial water pollutants and agricultural problems, which leads to risk the human health due to their contamination and potential toxicity (Li et al., 2014; Liang et al., 2017; Xu et al., 2014; Q. Yang et al., 2018)

Heavy metals pollutants are a result of the bad management of the sanitation of their industrial effluent and discharge them into the stream or river that will flow into the sea. Those irresponsible act will decrease the water quality and became a risk to the aquatic life also (Amoatey and Baawain, 2019). Heavy metals are a group of elements with higher water solubility and once released to the environment. It will be accumulated, especially in the food chain and the environment due to their persistency and non-biodegradable. The accumulation of heavy metals in the human body will result in many health risks such as organ failure, the shutdown of the nervous system, inhibited growth, cancer and in worst scenarios, lead to death (Rehman et al., 2018). The typical heavy metals element found as pollutants are arsenic (As), mercury (Hg), nickel (Ni), cadmium (Cd), copper (Cu), chromium (Cr), cobalt (Co) and zinc (Zn). Besides being water-soluble, those elements are well known as toxic and carcinogen.

Since the numbers of heavy metal pollution arise, the subject of removal of heavy metal is rapidly growing. As for now, there is ongoing research to get efficient methods for the removal of heavy metals from the water sources. The removal of heavy metals had been applied with several processes including chemical precipitation, solvent extraction, reverse osmosis, coagulation, cementation ion exchange or adsorption (Gunatilake, 2015). Some of these treatment processes such as chemical precipitation, ion exchange and electrochemical removal require a high-energy and will result in an incomplete removal and produce toxic sludge (Barakat, 2011). To find the best method, a process with a low-cost operation, and yielded higher heavy metals removal efficiency is needed. Thus, the adsorption technique has been identified as the most efficient technique when comparing with other removal processes.

Adsorption is a low-cost removal process which involves the transferring of the ions to the solid phase from the solution phase which technically the pollutant in the solution will flow into the sorbent, next it will adsorb on to the surface of the particles before being transferred within the sorbent particle. The adsorbent can be in any forms, from the commercial adsorbents such as activated carbon, silica gel, alumina, and natural adsorbents. Natural adsorbent, including the corn cob, natural zeolite, clay minerals and soils is obtained from the biological materials and the cost materials are comparatively cheap. The natural adsorbent is known as a porous structure with small particle size and larger surface area, where results in higher efficiency (Chakraborty et al., 2020).

A well-known low-cost natural adsorbent is a soil, which widely used in the adsorption process that acts as heavy metals removal. Soil comes in a small particle, with a large surface area, that brings higher value for removal of the heavy metals (Sangiumsak and Punrattanasin, 2014). The removal rate of heavy metals is increasing in line with the larger surface area of the soil used (Peng et al., 2017; Saeidi et al., 2015) claimed that one of the contributor factors that increase the removal process is due to the existence of iron oxide (Fe_2O_3) compounds in the soil. Iron oxide is naturally present in the in soil that widely being used in the water treatment process for several years. It has higher capability to adsorb, and provides as a host for the toxic elements with positive valence, during the adsorption process (Duncan and Owens, 2019; Scheinost, 2005)

The previous study executed by Mohd Fauzi, (2020), showed that there was significantly higher removal of lead (Pb) and cadmium (Cd) more than 75% after treated using three types of soils (sandy, red-earth soil, and clay soil). The sandy soil has the highest removal percentage, followed by the red earth and clay soils. This study is the continuation of the previous work done by Mohd Fauzi, (2020) but in a different aspect, in which she had discovered using the experimental way that sandy soil functioned well in removing the heavy metals from aqueous solution. Thus, this study continued with the physical way by characterizing the physical properties of the sandy soil, red-earth soil and sandy soil that used for the removal process.

1.2 Problem Statement

Water is the most crucial element for the living organism on earth. The freshwater supplies our daily activities, including drinking, industrial, and agricultural activities. In general, water demand has been increased due to the increasing population and expandable economic activities. The critical industrial process growing faster today that has led to another result, the problem of water pollution. These phenomena mainly cause the contamination of the water sources by the industrial effluents in terms of wastewater or chemicals effluent. The unethical dumping wastewater into the source of water will lead to pollution and become health risks to the human and other organism life.

One of the common pollutants identified is heavy metals. Heavy metals are a toxic and carcinogenic pollutant, with some of them were resulting from agricultural activities (such as Cu, Ni, Zn) with permissible amount limits and some of them used in industrial activities (Hg, Pb, As). The heavy metals being released to the streams by the removal of industrial wastewater, and excessive usage of fertilizers before being transported to the sea or deposited into marine life and sediments. Thus, it will join the food chains from our drinking to our food source from the aquatic organism. Since heavy metals are non-biodegradable and can be stored in living tissues, causing various diseases and disorders and thus they must be diminished or removed before discharging into the water body (Ahmaruzzaman, 2011).

There are various processes associated with the removal of heavy metals which have been introduced, especially when dealing with the industrial wastewater to safeguarding the water source. However, some of the removal methods require a higher cost, producing a lot of sludge and incomplete removal. Yet, the adsorption process has been identified as the best method that suits to overcome the problems stated, especially from the cost and the removal percentage perspectives. The usage of adsorbents had been widely used and increasing day by day since the availability and the low-cost production, where the natural adsorbent materials such as chitosan, zeolites, soil or clay are widely chosen for the adsorption process (Babel & Kurniawan, 2003).

However, this research interest is more focusing on the characteristics of the adsorbent itself that increase the efficiency of soil, which is used as the adsorbent (Mohd Fauzi, 2020). Fundamentally, the larger surface area of an adsorbent will increase the adsorption rate of heavy metals by providing a larger surface area for a successful adsorption process. Moreover, the past study reported that higher amount of naturally occurred (Fe_2O_3) in the soil facilitates the removal of heavy metals due to its metal-binding capabilities during the adsorption process. Thus, the physical properties of the different types of soil used by Mohd Fauzi (2020) were analyzed to exhibit their relationship as adsorbents for the removal of heavy metals in aqueous solution.

1.3 Research Objectives

1.3.1 General Objective

The main objective of this study was to investigate and relate the physicochemical characterization of the three types of soil (sandy, red-earth and clay soils) toward the removal of heavy metals from aqueous solution.

1.3.2 Specific Objectives

1. To exhibit the relationship of physical properties, the three types of soil with the removal of heavy metals from aqueous solution.
2. To identify the best soil provided for the removal process of the heavy metals based on its physicochemical properties.

1.4 Significance of the Study

This study provides useful information on the physical characteristics of the three types of soils in assisting the removal process of heavy metals from water sources. The characterization for each soil can be used to relate its physicochemical features with the efficiency of the heavy metal’s removal process. The critical point to our environment and living organism, to have a better place to live.

From this study, the best soil as a natural adsorbent in treating the heavy metals which is low-cost and straightforward could be suggested to the water treatment agencies and other industries that involved with wastewater management. The research on the removal of heavy metals will provide a crucial point to our environment and living organism, to have a better place to live.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the literature about heavy metals pollutants and their treatment in aqueous solution. To be specific, the methods more focusing on the treatments using three types of soils – red, sandy and clay types of soil. Besides, this chapter also reviews the advantages of adsorption methods to remove heavy metals from wastewater.

2.2 Heavy metals

Heavy metals are known as a group of elements that naturally occurred with characteristics of higher atomic mass and density. Usually, heavy metal has at least 5 g cm^{-3} in density and naturally occurred in the crust of our planet. There is a discussion on how to list out six types of definitions to heavy metals group – in terms of density, atomic weight, atomic number, and chemical properties. These definitions used before 1936 and the last one is the definitions without any apparent basis except the toxicity (Duffus, 2002) (H. Ali and Khan, 2018).

The most common of heavy metals include As, Pb, Cd, Cr, Cu, Ni, Zn, Mn and Hg. Some of the elements such as Zn, Cu, Fe, and Mn, are needed in our body as our nutrient's uptakes, to maintain the body function, somehow, the excesses of the dose of these elements may result to the acute and chronic toxicity.

2.2.1 Source of Heavy Metal

Heavy metals are the natural components inside the earth's crust, with their main feature are non-degradable. These heavy metals can be introduced in environments due to the natural activities such as volcanic eruptions, spring waters, erosion or various human activities including electroplating process, operations of mining extraction, or industrial usage of heavy metals as substances (S. Cheng, 2003; Huang et al., 2018)

Natural heavy metals are generally extracted from rock by each, soil, airborne dust and forest fires. These activities will occur naturally and affect the environment and the surrounding, including the water bodies and soil. A study in Iranian Industrial complex (Roozbahani et al., 2015) showed that there are soil samples found with higher contamination for Cu, Fe and Cd, and there is a higher amount of anthropogenic pollution to the soil compared to the natural one.The metal concentration is the highest at the industrial complex (88%) with a distance of 300 m from the pollution source (Roozbahani et al., 2015).

The human activities involved with the heavy metal's sources are electroplating, mining, and extraction operations. Fundamentally, electroplating consists of the process of deposition of thin layers of protection to a prepared surface of metals which categorized as the electrochemical process. The extraction of minerals compound from a mine area known as the mining process. It was focusing on physical separation and concentrated the mineral compound using physical and chemical techniques, which lead to waste productions. For example, gold mining produced significant waste called tailings which contain a considerable amount of heavy metals. The heavy metals will reach out to the environment, including air and water bodies (Fashola et al., 2016). The study for heavy metals from mining in Tibet, China found that the concentrations of Cu, As and Zn were exceeded the permissible limits both in the sediments and on the surface of the soils (Li et al., 2014).

Heavy metals typically occur in natural waters in trace quantities, but most are often toxic at deficient levels. The releasing to the water supplies will lead to severe health and environmental issues since those elements have non-bio-degradable and bioaccumulation tendency.

Bioaccumulation defines as the gradual accumulation process for any substances in a living organism (Borgå, 2013). It occurs when a living organism has a higher absorption rate than excretion (loss) rate of the substance from the body, which leads to the accumulation in the organism. Study in the freshwater of the food web in Cordoba which involved the survey of the different aquatic's samples found that plankton has the highest amount of bioaccumulation factor for Cu, Zn, As, Cd and Hg (Griboff et al., 2018).

2.2.2 Toxicity of Heavy Metal

The toxicity of heavy metals is influenced by several factors, including the age, gender, routes of exposure, genetics, nutrient factors, and the chemical species of the element. The most common heavy metals because of their high degree of toxicity such as cadmium (Cd), and lead (Pb). All of those elements are categorised under systemic toxicants which will affect to induce multiple organ damage, even at a lower dosage (Tchounwou et al., 2012). Some of the heavy metals such as Cd ions and PB ions are vital for the body of the water, but they can be toxic in larger dosage.

Cadmium (Cd) is a silver-white heavy metal which can be existed in the ore naturally. The primary usage of Cd is used in the electrode component of the alkaline batteries (Azeh Engwa et al., 2019). Besides, they also components in alloys and inside the polyvinyl chloride products and act as a stabilizer in paint colour pigments (Kawasaki et al., 2004). The emission route of Cd is thru an industrial process into the sewage sludge, fertilizers and groundwaters. In the agricultural activity, usage of fertilizers which contain Cd can remain them in soils and sediments up to several; decades before being taken up by the plants (Nogawa et al., 2004). Cd flowed from the rivers of pollutions area will go to the sea and affect the aquatic life through bioaccumulation (Amoatey and Baawain, 2019; Borgå, 2013; Griboff et al., 2018). Thus, the risk for health from Cd varies from plant to animal and finally to human as an apex predator.

One of the health risks of Cd toxicity is related to the function of the kidney. The chronic exposure will lead to the kidney to disrupt their role, to metabolite the calcium metabolism that will increase kidney stones and cancer (Casalino et al., 2002). The failure of the kidney will increase the high amount of calcium excretion in urine, which results in the significant decreases to the bones. This phenomenon will lead to bone-related diseases such as bone pain, osteomalacia, osteoporosis and *itai-itai* disease (Baba et al., 2013; James and Meliker, 2013). Cadmium is classified as Group 1 carcinogens for humans which may lead to the risk of ovarian cancer and breast cancer (Henson and Chedrese, 2004; Itoh et al., 2014; O. Yang et al., 2015)

Lead (Pb) has a slightly bluish with a form of bright silvery metal under a normal dry atmosphere. It can be found in our environments, which a lot was coming from human industrial activities such as burning fossil fuels, mining industrial and manufacturing process. Lead is massively applied as battery storage. Another usage is such as cable covers, plumbing and one of the elements in ammunitions. Besides, it also acts as a shield for X-ray radiation and nuclear-related machines due to its effectiveness as a sound and vibration absorber (Agency for Toxic Substances and Disease Registry, 2011).

Leads exposure will have a health risk to the children, especially from the playground near the lead-related industrial area (Wani et al., 2015). Lead poisoning will cause a child's health in terms of damages of the brain and nervous system (Cleveland et al., 2008; Klaassen et al., 1998), and retarded growth and development. Lead poisoning to children also will lead to poor academic performance (Bellinger, 2008), decrease in cognitive performance with additional associated with depression and anxiety disorder (Jacobs et al., 2002). The children will tend to become aggressive and having neurophysiological disorders such as attention deficit hyperactivity (ADHD) and antisocial behaviour (Sanders et al., 2009). The exposure to the lead also associated with the behaviour and emotional problems and may result in death at high levels (Al Osman et al., 2019).

2.3 Soil

Soil is a mixture of components consists of dead and living organisms (organic materials), minerals, air and soil solution. Soil is the surface mineral and/or organic layer of the earth which undergone some changes in physical, biological and chemical weathering. Soil is a complex material in the composition, which may vary for each location depends on their occurrence and properties. They are dynamic, changing behaviour in use and going spatial distribution since all their components are inhomogeneous and interact. (Soil Science Society of America, 2012)

Typically, soils composed of approximately 45% mineral, 5% organic matter, 20 – 30% water solution and 20 – 30% of air (Crouse, 2018). The mineral part is varied in shapes and sizes of particles with a different chemical composition. While the organic materials, including the plant and animal residues as long as the living organism. The soil solution or known as liquid phase is the aqueous area for various electrolytes moving in the soils. Most of them are nutrients for the plants (macro & micro), which differs in composition, and mobility from one pore to another pore of the soil. The gas (air) phase or soil atmosphere are having nitrogen (N_2), oxygen (O_2), water vapour and carbon dioxide (CO_2) with traces amount of other gases (Koorevaar et al., 1983)

Soil can be categorized into different types, with their distinctive characteristics, and contains several levels of details, vary from general to the specific to the part of the soil. The description of soil is a condition describing the physical appearance of the soil, as in-situ. It can be done, using physical examination, observation of the sampling area and the history of geological of the places. It can be in the form of the texture, the colour, the presence of organic materials, and the size of the constituent. The classification of soil was determined based on the separation into the classes or groups which shared the same characteristic or nearly similar behaviour. The type is done after a thorough examination with the aid of mechanical instruments, such as permeability, stiffness and strength, porosity, and the pore size (Davison and Springman, 2000)

2.3.1 Soil Characteristic

There are many properties in soils to define their characteristics, to state their state and groups. The typical three categories used to describe the soil characteristics are physical, chemical and biological properties. Chemical differentiation of the soil can be based on several factors. The specific measurement of chemical properties needs to be done by the aid of chemical appliance and applications.

Physical properties usually will explain the structural and water movement of the water or air in the soil. It will also touch the easiness to dig the soil from its place. Soil texture is one of the features used to describe the different size of mineral particles. Texture refers to the sizes of the individual particles, excluding the gravel and stones. Soil texture can be differentiated by the amount of sand, silt and clay, that will be efficiently looked under the high-powered microscope. From the dominating particles size, it can be categorized into sand, clay, silt, peat, chalk, and loam types (Boughton, 2020)

Structural of soil defines how the soil particles clumped together to form a structure. In these properties, the organic matter and soil organism play their role to influence the soil structure. Structure of the soil essential to regulate and retention of air and water in the soil will affect the nutrient availability (Rai et al., 2017; USDA, 1996)

Soil porosity refers to the pores within the soil, which affect water and air movement and retention in the soil. The goods and healthy soils have many pores in between of the particles, while low-quality soils have fem pores, or cracks (Finch et al., 2014). Some soil porosity will be affected by the human activities, that will alter the porosity the soil. The porosity will affect the surface area of the soil. Since the smaller size of the pore, the larger surface area will be produced. Thus, for both characteristics can be done simultaneously, by using two different equipment (Danielson and Sutherland, 1986)

The main characteristic focuses on the organic matter content of the soils and the cation exchange capacity. Organic matter contents in the soils refer to the dead plant and the presence of decomposed material of (micro)organism (Durães et al., 2018). The decomposed materials will make way for recycling of the nutrient and measuring the fertility of the soil. Organic matter is commonly measured to the total carbon since it refers to the organic compound, which consists of primary carbon. The chemical analysis can also do to differentiate the organic content of each soil (Cox et al., 2000; Margenot et al., 2016)

The organic material in the soil is carrying the negative charges, while water in the soil dissolves the nutrients and other chemicals. The cation in nutrients such as, potassium, ammonium and metal oxides brought the positive charges and attracted to the negative charges of any mineral matter, that will lead to the higher adsorption properties of the soils. Thus, the presence of positive cation charge mostly metal to retain the minerals being adsorbed on to the soil (Parfitt, 1979; Ron Goldy, 2013)

2.3.2 Types of Soil

Types of soil can be determined at the early stages of physical examination of the soils. It can be the group in terms of the particles within a soil which consists of sandy, clay, silt, peak, chalk and loam types. Sandy is a light type of soil, a warm and dry structure and chemically tend to be acidic and low of nutrients inside of the soils. It is often known as a lighter compared to any other type of soils, due to their composition higher in the sand and a little volume of clay (Boughton, 2020). Clay soil is a heavier soil that has a higher number of nutrients. It can remain wet and cold both in winter and dry out weather. It made of over 25 % of clay, and it has small pores between the particles which leads to the high volume of water (Crouse, 2018)

The soil colour observation is one types of physical examinations. Soil colour can be in a range of black to the red and white. It is usually coming from organic matter and iron in the soils. It varies with parent material, the duration the soil has been forming and the surrounding of the environment itself. The black colour soil is linked to the higher levels of organic matters, while the pale soil usually the sign of washed out. The red-earth soil is indicating good drainage that contains higher oxygen content. The higher oxygen tends the soil to develop a rusty colour and maybe darker due to the organic matter (R. S. Jackson, 2014)

2.3.3 Characterization of Soil

Characterization of the soils can be done using several instruments. Field Emission Scanning Electron Microscopy was used to characterize the samples to look out for their morphological structures. The FESEM was useful for analyzing the structure of the soils and the size of the pore under the high magnification microscope. While EDX that equipped together doing the elemental analysis for each sample by composition percentage in atomic and weight. Thus, in FESEM / EDX, we can analyze the morphological structures of the soil and their elemental composition. (Doménech-Carbó et al., 2019; Eisazadeh et al., 2013; Wahab et al., 2017)

Characterization of the soil in terms of their mineral component can be done using instruments Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectroscopy is a unique instrument that can analyze the elemental composition of the soil sample. It offers complementary techniques to evaluate their soil components. The methods vary from as common as transmission, with two other methods called Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Attenuated Total Reflectance (ATR). FTIR spectroscopy is very useful to characterize the soil organic matter (SOM) with the presence of the peak of the functional group. (Cox et al., 2000; Margenot et al., 2016)

Brunauer, Emmet and Teller (BET) analysis has been used to determine the specific surface area of the sample given. From the surface area, it can be used to predict the dissolution rate, which proportion to the specific surface area. The surface area of the sample being calculated when the adsorption of N2 gas on the solid and the amount of adsorbate gas lining to form a monomolecular layer on the surface. (Eisazadeh et al., 2013; Feller et al., 1992)

2.4 Heavy Metal Removal

Nowadays, the treatment of heavy metals pollution is the main priority to the industrial players as they are growing more severe years by years in combating the environmental smog. Thus, these toxic heavy metals from their industrial area or municipal area are needed to be removed before being transported to the water sources to protect the environment and health of the living organism. There are many heavy metals removal methods such as chemical precipitation, redox reaction, ion-exchange, membrane filtration, electrochemical treatment, reverse osmosis, evaporative recovery and solvent extraction. However, these conventional methods which always being used have their advantages and drawbacks such as costly, incomplete heavy metals removal, high capacity energy requirements, the production of side products such as toxic sludge or other waste products (Gupta et al., 2010).

2.4.1 Chemical Precipitation

The chemical precipitation is one of the well-known effective ways to remove heavy metals from wastewater. The concept behind this method is the transformation of materials dissolved in water into the solid form. The ionic components from water are extracted by adding counter-ion to minimize solubility. This treatment is used most widely in the metal plating industry, to remove the heavy metals in water and wastewater solutions (Lawrence K. Wang, David A. Vaccari, Yan Li, 2005).

The precipitation technique has been tested for removal on Pb(II) and Zn(II) by using two porous rock samples, (limestone and rhyolite tuff) both in cylindrical and powder forms. Németh et al., (2016) found that the Pb (II) and Zn (II) were precipitated from the sample solutions (most probably in hydroxide form) and stuck to the surface materials of the host rock minerals and the pores. This could conclude that both porous rocks not only remove the heavy metals by adsorption but also using the precipitation concepts.

In another study, the chemical precipitation was more effective compared to electrocoagulation in removal metals from acidic soil leachate (ASL) in low contamination levels of Pb (30 mg^{-1}) and Zn (18 mg^{-1}). The chemical precipitation experiments were done by Meunier *et al.* (2006) was determined using calcium hydroxide or sodium hydroxide. Another study used this method to remove Pb from the thermal stabilizer by using a natural coagulant (nopal mucilage of cactus). The research has shown there was a reduction to 1.76 mg/L from the original lead concentration (51.68 mg/L) (Curo and Valverde Flores, 2017)

2.4.2 Redox Reaction

A reaction to oxidation-reduction (redox) is a type of chemical reaction which involves electron transfer between the two species. It is a process of transferring of electrons which leads to changes in oxidation stated either increasing or decreasing. The redox reaction water treatment process depends on several factors such as pH, redox conditions, temperature, moisture or any that gives influences of the heavy metals group such as toxicity, mobility and the reactivity (Lichtfouse et al., 2015).

In a study done by Yang et al. (2018), they focused on the usage of the controllable redox reaction of birnessite as a method for the removal of Cu^{2+} from water. The analysis was done by multi-cycle electrochemical redox reaction and found that the capacity of electrosorption increased up to 372.3 mg/g. The increment of adsorption capacity for Cu^{2+} could be derived from the changes in chemical composition and the dissolution recrystallization process of birnessite during electrochemical redox reactions. Another usage of birnessite, a layer structured was in the study by Liu et al., (2019) to enhance the adsorption of Cd^{2+}. They used three types of tunnel-structured manganese oxides (pyrolusite, cryptomelane and todorkite) for the electrochemical adsorption of Cd2+. The result shown that the adsorption capacity of Cd^{2+} follows by order of cryptomelane > todorekite > pyrolusite with the highest adsorption capacity reaches 192.0 mg g^{-1}.

2.4.3 Ion-exchange Method

Ion exchange is a reversible chemical reaction which substitutes the ions from the wastewater solution with the similar charge ion that attached to the immobile solid particle. In the water treatment process, ion exchange soluble ions in solution will be attracted to the solid phase. The process will be used to remove metal ion in the solution which contains the special ion exchange. The most common ion exchangers are synthetic organic ion exchange resin have used reduce graphene oxide grafted by 4-sulfophenykazo groups (ROGS) in suggesting two different kinds of adsorption, ion exchanges and coordination (Chaemiso and Nefo, 2019; C. Z. Zhang et al., 2018). The mechanism was used on heavy metals of Pb(II), Cu(II), Ni(II), Cd(II) and Cr(III) with the equilibrium, not more than 10 minutes. From the study found that for Pb(II), Cd(II) and Cr(III), the adsorption of RGOS attributed to the coordinate reaction between N atoms and heavy metal ions, and ion exchange involves Na+ in sodium sulfonate and heavy metals. Based on EA data and FT-IR spectra, the adsorption was achieved. Meanwhile, the study was done by Zewail and Yousef, (2015), used the spouted bed with AMBERJET 1200 Na resin to remove the Ni and Pb from wastewater, showing that the removal achieved for 99% and 98% removal for Pb and Ni respectively. In the same study, they set the different parameters to be investigated such as type of heavy metal ions, contact time, superficial air velocity and initial heavy metal ion concentration on percentage heavy metal ion removal.

2.4.4 Membrane Filtration

Membrane filtration is one of the removal processes, which is useful to remove the solid suspension organic compounds and inorganic elements such as heavy metals (Gunatilake, 2015). There are various types of membrane filtration can be utilized such as ultrafiltration (UF), nanofiltration, microfiltration, electrodialysis and reverse osmosis type that differs in pore structure, membrane permeability and operating procedures applied ((Murthy and Chaudhari, 2009).

Ali et al., (2017) investigate the usage of low-cost ceramic membrane filtration for removal of three types of heavy metals (Pb, Cu and Cd). The ceramic membranes built from low-cost materials of local clay mixed with different percentage of sawdust (0.5%, 2.0% and 5.0%) with 15 x 15 cm dimensions with 2cm thickness. The study found that the removal of three types of heavy meals for those types of filtration increased up to 99% efficiency. In another study of removal of aluminium from wastewater, found out that both nanofiltration and reverse osmosis (RO) effectively removes aluminium, total chromium and nickel more than 90% from the wastewater effluent production. At 20 bar operating pressure, RO (SW30) showing slightly higher conductivity removal values (90%) compared to NF 270 membrane with 87% (Ates and Uzal, 2018).

2.4.5 Adsorption

Adsorption is one of the removal techniques that very useful to remove the contaminants from waters and wastewater. It is a treatment process which involves physicochemical reactions with the most preferred and efficient choice. (Chaemiso and Nefo, 2019). The adsorption process involves a mass transfer process and substances which bind to physical and chemical interactions to a solid surface. Due to the simple design and easier to operate, the adsorption method is one of the removal technique from water and effluents to control the pollution and wastewater management (De Andrade et al., 2018).

Different forms of adsorbents may be used for heavy metal removal using the adsorption technique. Recently, several researchers have been investigating the potential low-cost absorbent in wastewater heavy metal ions. An example of adsorbents for the elimination of heavy metals from water supplies has been studied, such as agricultural waste, manufacturing by-products and waste and natural adsorbents (Barakat, 2011).

The common adsorbent being used is activated carbons. Al-Malack and Dauda, (2017) studied the activated carbon, a precursor from sewage sludge can be used to uptake phenol and cadmium from aqueous solutions. They found out that the activated carbon with the surface area of 300 $mg^2\ g^{-1}$ tends to adsorb more phenol than Cd^{2+}. They also suggested that the activated carbon can become from a sludge that will benefit the wastes management of industrial solids together with the treatments of phenols and cadmium in water.

Other than that, there is study concentrated on using graphene/activated carbon (GAC as an adsorbent for Pb(II). The usage of GAC which developed from graphene oxide and glucose have mesoporous structure and surface area 2012 $m^2\ g^{-1}$ with a pore volume of 1.61 $cm^3\ g^{-1}$. This study result showed the maximum capacity for adsorption of Pb(II) was 217 mg g-1, higher value when comparing to any other adsorbents (Saeidi et al., 2015).

With referring to the industrial waste as adsorbents, Bhatti et al., (2017) suggested the cost-effective adsorbents from the waste tire. These adsorbents had capacities for treatment up to 105 and 174 mg g^{-1} for Cr(VI) and Cr(III), respectively in their optimum conditions. The adsorption using waste tire also able to remove 80% of the Cr species in a tannery waste. Thus, the usage of waste tire benefits in term of saving the environment from the waste products and the new application for the treatment of tannery effluents.

On the contrary, several researchers have researched the effectiveness of many cheap materials as natural adsorbents due to its environmentally friendly, higher efficient and abundant. Those cheap adsorbent materials include natural mineral (clays), agricultural waste (peels, nutshells, husks), animal waste (eggshells), forest waste and industrial waste (eggshells) (Chaemiso and Nefo, 2019; Esmaeili et al., 2019; Gunatilake, 2015; İnce and Kaplan İnce, 2017; Khan et al., 2019; Tran et al., 2016). However, the adsorption capacity of these different materials used for the removal of heavy metal presented a high sensitivity towards the variation of temperature and pH (Chakraborty et al., 2020).

Zeolite is a type of natural materials that can be used as an adsorbent for heavy metal treatment. It is a low-cost process, easy to obtain, and their capacity can be enhanced to increase the effectiveness. Zeolites sorbents have both ion exchange and sorption properties that very useful for removal of heavy metal. There are three kinds of zeolites, including natural modified and synthetic zeolites. Modified zeolites and synthetic zeolites have higher sorption performance and cation exchange (Yuna, 2016). Natural and modified zeolites have been tested to Pb, Zn, Hg and Mn with optimum pH > 3.8, found out their content had been decreased in the wastewater (Kragović et al., 2018)

2.5 Soil Adsorption

Soil is a known one of the adsorbents that very useful for the heavy metals' adsorption. Soils can adsorb the metals ion from their solutions that play an essential role both in agriculture elements (as fertility) and the environmental treatment use. Many studies have been conducted to utilize the use of soil and the presence of metals as the absorbent of the heavy metal treatment (Eisazadeh et al., 2013; Mellis et al., 2004; Van Benschoten et al., 1994). It is a unique characteristic for adsorption of heavy metals since they have inorganic colloids and organic colloids matter that useful for heavy metal adsorption.

In the year of 2013, Ouadjenia-Marouf et al. conducted a study to find out the possibility of using the silt to remove the heavy metal elements from aqueous solutions. The silt which was taken from Chorfa dam, at the area of Mascara, western Algeria, found out that, 95% and 94% of Cr and Cu were removed from aqueous solution, respectively. In comparison, the concentrations of Cd were decreased by 45%.

On 2019, there was a study conducted to study the removal of heavy metals by using different types of soils (Wazwaz et al., 2019). Samples of soils taken from the other areas of Oman, with the natural adsorbent used were, silty soil, sandy soil, and clay soil. The results for this study showed that the highest adsorption for Cu, Zn, Mn and Cr was clay soil with percentage removal of 76.85% for Cu, 88.61% for Zn, 82.99% for Mn and 31.19% for Cr which defeated another two types of soil.

In Nigeria, the study was conducted to investigate the properties of adsorption of clay soil which abundance in Ire-Ekti area. Damilolakayode et al., (2019) used raw clays to remove four types of heavy metals from aqueous solution. The result turned out that the adsorption capacity of clay for heavy metals used as followed; Pb > Cu > Cr > Ni with each percentage removal stated 99.3, 80, 70.9 and 68.7%, respectively.

Mohd Fauzi, (2020) executed a study to differentiate the adsorption percentage of heavy metals by using three different types of soil, namely red-earth, clay and sandy. From the experiment conducted, the optimum condition for adsorbent was using 5 g in 100 mL of adsorbent with 10 to 30 minutes of contact time in ambient temperature. Results shown that the highest removal of heavy metal was sandy soil, followed by red-earth soil and clay soil.

CHAPTER 3

METHODOLOGY

3.1 Apparatus and Instrument

The list of apparatus and instrument used in this study, as shown in Table 3.1 and 3.2.

Table 3.1 List of Apparatus

Apparatus	Brand
Spatula	-
Petri Dish	-
Fill Glass	-
Funnel	-
Grinder	-

Table 3.2 List of Instruments

Instruments	Brand
FESEM	Quanta
FTIR	Bruker Tensor 27
BET	Quantachrome Autosorb iQ3
Hot Air Oven	Protech
Weighing Balance	Sartorius AX 224

3.2 Sample Collection

Three types of soil were collected at various locations around the Machang district, Kelantan. The types of soils collected were clay soils, red-earth soil and sandy soil. For a collection of clay soil, the sample was taken at the paddy field, near to Kampung Simpol Machang, Kelantan. The sample for sandy soil was taken from an abandoned area located in Kampung Kepas, Machang, Kelantan. While for red-earth soil, the sample was collected at the paddy field, also located at Kampung Simpol, Machang, Kelantan. For each location of the sampling site, the approximate area was measured and determined. The collected soil samples were free from contamination, and any crop residue found at the sample soils were removed. Soil samples were taken for each site by using a soil sampler and following soil sampling guidelines (Jason P. Ackerson, 2018).

The collected samples of the soils continued until the sufficient amount. Each different types of soil were mixed thoroughly to form a homogenous mixture before stored in the sealed lock plastic bag. The samples are taken then was labelled for each packaging following the types and date/time taken. The appropriate measures were taken to avoid any contamination or introduction areas between the samples taken. Soils were taken with a different sampler to prevent cross-contamination. In this study, only 20 cm of the depth of collected soil was considered for the characterization process since the similar performance with 40 cm collected soil in removing heavy metals from aqueous solution.

3.3 Sample Preparation

After the sampling process, any residue or unwanted materials were removed from the samples of the soils taken. Then, each of the samples was put on the petri dish and dried under the temperature of 60°C. Finally, all of the samples were ground into a powder form using the grinder.

3.4 Field Emission Scanning Electron Microscope (FESEM)

Structural morphology of the three types of soil was examined under the Field Emission Scanning Electron Microscope (FESEM, Zeiss, Quanta) with the energy of 10.0 kV coupled with EDX analyzer (FESEM-EDX). The elemental composition on the submicron scale of the soils was determined by using Energy Dispersive Xray (EDX). The sample was mounted on the platform called stub coating with a gold sputter—the sample images captured under the operating condition of 10.0kV.

The FESEM is a microscope with an ultra-high-resolution that works instead of light with negative electrons emitted from a field source of emission. The object is scanned in a zigzag pattern by electrons. FESEM equipped with the X-ray energy dispersive spectroscopy was used to differentiate for the three types of soils in terms of – porous structures or morphology, and the elements constitute in each of the soils.

3.5 Fourier-transform Infrared (FT-IR) Spectroscopy

FT-IR spectroscopy was used in this study to determine the existence of a functional group in all soil samples. The infra-red spectra of the three types of soils were determined by using a Bruker Tensor 27 FTIR Spectrophotometer. The soil samples were pressed into a KBr pellet and inserted into the FTIR spectrophotometer with the sample holder. The samples were analyzed for 4000 to 800 cm^{-1} and recorded by FT-IR using Nicolet Omnic software. By comparing the standard reference for each peak, the chemical bond of the sample was determined, which assigned the functional group present in the sample.