CHICKEN FEATHER FIBRES AS AN ADSORBENT IN TREATING HEAVY METAL

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By

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I hereby declare that all corrections and comments made by the supervisor(s) and examiner have been taken into consideration and rectified accordingly.

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ABSTRAK

Bulu ayam yang merupakan produk sisa dari ladang ternakan dalam rawatan air sisa telah menarik minat dari banyak penyelidik. Kajian ini hanya memberi tumpuan kepada serat bulu ayam sebagai bahan penyerap yang disediakan oleh rawatan kimia untuk menyingkirkan logam berat dari air buangan sintetik. Dalam usaha meningkatkan kapasiti penjerapan Mangan (Mn) dan Zink (Zn), penyediaan bulu ayam yang telah diubahsuai secara kimia (CMCF) dilakukan dengan beberapa kaedah. Pertama, bulu ayam telah diubah suai dan dirawat dengan larutan NaOH berair pada kepekatan yang berbeza. Ini untuk menjelaskan perubahan struktur dan morfologi bulu ayam (CFs). Selanjutnya, serpihan keratin yang terlarut boleh dikembalikan semula ke permukaan CF dengan tindak balas silang yang menghubungkan dengan Epichlorohydrin (Epi) dalam larutan NaOH berair, yang akan dinamakan sebagai adsorben Epi / CF, dan akhirnya CFs berfungsi dengan Ethylenediamine (EA) dalam larutan NaOH berair oleh Epi cross-links. Pencirian telah dilakukan menggunakan kaedah yang berbeza iaitu SEM-EDX, BET dan FTIR. SEM-EDX telah dilakukan untuk menyiasat struktur dan sifat CMCFs. CFs yang dirawat NaOH pada kepekatan yang berbeza didapati sama dalam struktur dan sifat antara satu sama lain manakala Epi / CF dan EAEpi / CF menunjukkan perbezaan yang ketara. BET pula telah dilakukan untuk menentukan saiz liang permukaan CMCFs. Selain itu, analisis elemen bulu ayam dilakukan oleh FTIR. CF yang dirawat NaOH telah diperhatikan mempunyai kapasiti penjerapan yang lebih baik berbanding dengan penyerap Epi / CF dan EAEpi / CF semasa penyingkiran logam berat. Oleh itu, bagi kedua-dua penyingkiran logam berat, NaOH-0.2 / CF telah dipilih sebagai yang terbaik penyerap dengan keupayaan penyingkiran 100% untuk kedua-dua Mn dan Zn. Oleh itu, keputusan yang diperolehi daripada kajian pengoptimuman yang dilakukan dengan menggunakan NaOH-0.2 / CF sebagai penyerap terbaik, pada keadaan optimum; 0.50 g

jisim adsorben, 23.64 jam waktu hubungan dan pada kepekatan logam berat yang 5.33 mg / l menunjukkan bahawa model yang diramalkan adalah sah untuk digunakan dalam sistem sebenar bagi kedua-dua logam berat, kesilapan dan sisihan piawai yang dikira adalah di bawah 1. Isotherm penjerapan keseimbangan untuk CMCFs kebanyakannya sesuai dengan model Langmuir untuk penyingkiran Mn (R2 ≈ 0.9) manakala untuk penyingkiran Zn (R2 ≈ 0.8), proses penjerapan mengikuti Freundlich. Ini bermakna bahawa proses penjerapan Mn menggunakan CMCFs adalah penjerapan kimia dan bahawa untuk Zn ialah penjerapan Fizikal. Secara keseluruhan, kajian ini membuktikan bahawa CF diubah suai mempunyai potensi yang baik untuk digunakan sebagai penyerap untuk mengeluarkan logam berat.

ABSTRACT

The chicken feather which is a waste product from poultry farm in wastewater treatment has attracts interest from many researchers. This study only focussed on chicken feather fibres as an adsorbent which was prepared by chemical treatment for the removal of heavy metal from the synthetic wastewater. In the purpose of improving the adsorption capacity of Manganese (Mn) and Zinc (Zn), the preparation of chemically modified chicken feather (CMCFs) was done by several methods. First, the chicken feathers were modified and treated with aqueous NaOH solution at different concentrations. This is to clarify the changes in the structure and morphology of chicken feathers (CFs). Next, the dissolved keratin fragments could be rejoined back to the CFs surface by the cross-linking reaction with Epichlorohydrin (Epi) in aqueous NaOH solution, which will be named as Epi/CF adsorbent, and lastly CFs were functionalized with Ethylenediamine (EA) in aqueous NaOH solution by Epi cross-links. The characterization was done using different methods which is SEM-EDX, BET and FTIR. SEM-EDX was done to investigate the structure and properties of CMCFs. NaOH-treated CFs at different concentration were found to be similar in structure and properties to each other while Epi/CF and EAEpi/CF shows significant differences. BET was done to determine surface pore size of CMCFs. The elemental analysis of the chicken feathers was done by FTIR. NaOH-treated CFs have been observed to have better adsorption capacities compared to Epi/CF and EAEpi/CF adsorbents during the removal of heavy metals.. Hence, for both removals of heavy metals, NaOH-0.2/CF has been chosen as the best adsorbent with removal capabilities of 100% for both Mn and Zn. Thus, the result obtained from the optimization study done by using NaOH-0.2/CF as the best adsorbent, at the optimum condition; 0.50 g mass of adsorbent, 23.64 hrs contact time and at the concentration of heavy metals which is 5.33 mg/l shows that the predicted model is valid

to be applied in the actual system as for both heavy metals, the error and standard deviation calculated is below 1. The equilibrium adsorption isotherm for the CMCFs mostly fit the Langmuir model for the removal of Mn ($R^2 \approx 0.9$) while for the Zn removal ($R^2 \approx 0.8$), the adsorption process follows Freundlich. This means that the adsorption process of Mn using CMCFs is chemisorptions and that for Zn is physisorptions Overall, this study proved that the modified CF has a good potential to be used as an adsorbent to remove the heavy metal.

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LIST OF ABBREVIATIONS

Symbol	Description
ANOVA	Analysis of Variance
BET	Brunauer–Emmett–Teller
C	Carbon
CCD	Central composite design
CF	Chicken feather
CFF	Chicken feather fiber
CMCF	Chemically modified chicken feather
COD	Chemical Oxygen Demand
C_o	Initial concentration
C_e	Equilibrium concentration
EDX	Energy-dispersive X-ray spectroscopy
EA	Ethylenediamine
Epi	Epichlorohydrin
FTIR	Fourier-transform infrared spectroscopy
g	Gram
H	Hydrogen
h	Hour
K	Kelvin
K_L	Langmuir constant related to rate of adsorption
K_F	Freundlich capacity factor
L	Litre
Mn	Manganese

m^3	Cubic metre
mg	Milligram
ml	Millilitre
mol	Mole
N	Nitrogen
O	Oxygen
RSM	Response Surface Methodology
rpm	Revolutions per minute
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent
q_{max}	Langmuir constant related to maximum adsorption capacity
R^2	Coefficient of determination
S	Sulphur
SEM	Scanning electron microscope
T	Temperature
t	Time
V	Volume of sample
W	Mass of adsorbent used
Zn	Zinc
1/n	Freundlich intensity parameter
µm	Micrometer
°C	Degree Celsius
%	Percent

CHAPTER 1

INTRODUCTION

1.1 Background Study

Pollution is becoming a concern in a modern world that we live in today. Industrial, agricultural and domestic activities are the main contributor to the environmental pollution. These pollution are released into the water bodies such as rivers, lakes, ocean, and groundwater. In recent years, water pollution with heavy metal has become an important environmental threat mainly because of the numerous industrial effluent containing these and other pollutant. Heavy metal are highly toxic non-biodegradable, and tend to accumulate causing several diseases and health disorders in human, and other living organisms (Rosa et al. 2008).

The level of water quality in Malaysia is not bad as many other developing countries in the world. However, the water bodies such as rivers are mainly polluted due to point and non-point pollution sources. Domestic and industrial wastewaters are the main point sources responsible for degraded river water. Based on the monitoring done by the Department of Environment (DOE) of point sources, it shows that there are significant amount of pollutants which contributed by both untreated sullage and from storm runoff. The non-point pollution source accumulates from various different sources and affect water body. Based on the study on the national urban runoff (NURP) in the USA, non-point pollution sources plays a significant role in the degradation of water quality (USEPA, 2009). The non-point pollution sources are generally more complex as compared to the point pollution sources. Department of Drainage and Irrigation (DID) have indicated that the most common pollutant responsible for water pollution are mainly released from the non-point pollution sources. This happen due to the improper sanitary system in suburban areas.

Car wash stations are categorized as non-point pollution sources where this domestic sewage contributed high amount of pollutant into the river (Silva et al., 2017). Carwash stations in the cities used the tap water to wash vehicles without recycling. The carwash service stations produce high amount of wastewater which is about 150 to 300 litre per day (Hashim & Zayadi, 2016). Car wash wastewater comprises oils, elements from brake linings, rust, trace amounts of possibly chromium and soap that are commonly used to wash the cars introduces phenols, dyes, acids, and ammonia (Zayadi et al., 2015). Moreover, car wash contains oily wastewater with toxic substances such as phenols, polyaromatic hydrocarbons, which are inhibitory to plant and animal growth, equally mutagenic and carcinogenic to human beings. There are many particles and chemicals have been found in carwash wastewater. Hence, the concentration and the severity of each element should be assessed in treating the pollutant.

The discharge for carwash stations also contains heavy metal such as copper, silver, iron, zinc, manganese, and others (Gunatilake, 2015). The discharge of these heavy metal had caused various effect towards the human and flora and fauna. However, there are some heavy metal which are grouped as important elements for human, animal, and plant but when consume in large amount, they happened to be toxic to the consumers. Thus, effective recycling and reuse of carwash wastewater by the suitable treatment processes can preserve a huge amount of carwash wastewater which used to be discharged.

A proper and effective treatment need to be carried out in order to treat the wastewater. There are various method in treating the wastewater such as physical method which consist of surface degreasing, sand filtration, activated carbon adsorption, or membrane separation (Tu et al., 2009; Moazzem et al., 2018). However, these treatment are not effective in term of cost. Recently, some studies have shown that the wastes from the processing industry are rich in fibrous protein which is suitable to be converted as an adsorbent in treating the wastewater. Remarkably, chicken feathers which contain about 90 percent of protein can be considered as cheaper alternative compare to other treatment process and also a renewable source of protein fibre which can be converted into low cost adsorbent (Khosa et al., 2013). Furthermore, a lot of researchers have proved that chicken feather have the potential to be used as and adsorbent due to its keratin composition.

1.2 Problem Statement

The increasing number of cars is a result of improvement in quality of life and well-being (Baddor et al., 2014). This condition has intensively contributes in the growth of commercial carwash stations. Here, the increasing numbers of carwash stations cause deterioration of the quality of river water. This is due to carwash wastewater is indirectly contribute the sources in polluting the river (Aikins & Boakye,b 2015). Commonly, the wastewater from these premises contains oil and grease, carbon, detergents, heavy metals, acids organic and inorganic matter. Thus, all these hazardous pollutants may cause adverse effects towards aquatic life if its end up in river water.

This wastewater should be discharge into sewerage system and treated in sewage treatment plant. However, ignorance by the car wash shop operators regarding this issue, the wastewater from these premises act as surface runoff and end up in river. Heavy metals are the most concerning pollutant considering their non-destructive nature and toxicity (Kumari et al., 2011). Due to that, treatment of carwash wastewater is important before the effluent can be discharged into the river. There are a lot of treatment methods that have been used to remove heavy metals such as oxidation, reduction, reverse osmosis, coagulation and adsorption (Ihsanullah et al., 2016). However, adsorption process which is mostly used in wastewater treatment plant is considered to be one of the appropriate methods in term of capital and operating cost. However, this method is highly depend on the adsorbent that will be used. There are many types of adsorbent and the selection of the adsorbent is based on the adsorbate (pollutants) that are targeted to be removed.

Nowadays, there are many research conducted to produce a low cost and sustainable adsorbent. Here, the materials that are used to make the absorbent are mostly come from the waste materials. Currently, the focusing on the chicken feather as an adsorbent has attracted the attention of the researcher due to its low cost as well as its properties. This is due to the chicken feathers are composed mainly of keratin which is a kind of self-organized protein. Here, it shows that chicken feather fibre has the potential to be used as an adsorbent. In order to use the chicken feather as an adsorbent, the modification of the properties need to be carried out. This modification involved chemical or physical treatment.

As aforementioned of the problem, this research is to study the adsorption for Zn and Mn from synthetic wastewater by using chemically modified chicken feather fibre as an absorbent. Therefore, this experimental work will based on the Ping et al., 2009 with some modification. This research will be highlighted on the suitability of chemical activation method of CFF to remove heavy metal from the synthetic wastewater prepared based on carwash characteristics.

1.3 Aims and Objectives of study

The main focus of the study is to examine the characteristics of chicken feather fibres before and after chemical treatment, as well as converting the chicken feather fibres to a promising and cheap alternative material for wastewater treatment regarding its adsorption technique to remove the pollutants. The objectives of this study are as below:

1. To determine the characteristic of the chicken feather by chemical treatment.
2. To study the capability of the chicken feather fibre as an adsorbent to remove Zn and Mn.
3. To determine the adsorption isotherm value Zn and Mn removal and kinetic study.

1.4 Scope of study

Activated carbon is used as a primary adsorbent in wastewater treatment. The main objective in this study is to examine the effective approach to activate the keratin fibre to be used as an adsorbent. The activated chicken feather fibres will be studies on its adsorption performance synthesizing, analysing and measuring the efficiency and the capacity of the heavy metals removal.

The efficiency of the activated chicken feather fibre (CFF) was evaluated through chemical process on the chicken feather fibre (CFF) itself for the removal of heavy metal ions in the synthetic wastewater prepared based on the carwash characteristics. Three different alkaline treatment which is sodium hydroxide, epichlorohydrin and ethylenediamine will be carried out and the most promising method will be chosen as the main constituent to modify the CFF.

The characterization of chicken feather fibre (CFF) will be carried out by using SEM-EDX/BET/FTIR to study the morphology, compound, surface pore size and the elemental analysis (chemical activation) before and after the treatment.

The batch experimental study was conducted to determine the capacity and effectiveness of adsorbent on the heavy metals removal. This batch study will help determine the best approach of chemical activation. Data analysis was carried out by ANOVA to determine the interactions between variables and responses. Adsorption kinetic study, adsorption mechanism study and adsorption isotherm study are carried out after the determination of both zinc and manganese and the best adsorbent is chosen for the optimization process.

CHAPTER 2

LITERATURE REVIEW

2.1 Background study

The increasing of both the economy and the improvement of human life have affected and threatening the environment. Wastewater discharged from the municipal, industrial, and commercial sectors have serious effect on the environment. The wastewater from these three sectors consist of various heavy metal. The exposure to heavy metal may cause serious health problems even at a very low concentration. The main sources of heavy metals are the wastewater from modern chemical industries such as chemical industries such as battery manufacturing, fertilizer, mining paper and pesticides, metal plating facilities, metallurgical, mining, fossil fuel, tannery and production of different plastics such as polyvinyl chloride (Ihsanullah et al., 2016). The commercial business especially carwash stations are also involved in polluting the environment. Car that were washed in the street can pollute streams, rivers, bays and estuaries due to accumulated sediments will flow to gutter system and go into storm water system without undergo any treatment. Hence, endangered the ecosystem when washes away to the drainage system, streams and to the receiving waters, causing and lead to the increased environment pollution (Hashim & Zayadi, 2016).

Therefore, the removal of heavy metal is extremely important. Numerous technologies had been used to treat the wastewater contaminated by heavy metals. However, adsorption is the most widely method used in wastewater treatment which were based on the physical interaction between sorbents and metal ions. Adsorption is considered to be very suitable for wastewater treatment due to its simplicity and cost effectiveness (Lakherwal, 2014). In the recent years, there are a lot of researchers studying and developing a low cost adsorbents. Common material which is chicken feather fibre has been investigated on the on its morphological structure as a low cost adsorbent with the different activation methods. Chicken feather fibre which is rich in keratin plays an important role in converting the chicken feather to added-value products such as livestock feed (King'ori, 2012), in leather tanning (Sila et al., 2015) and as biocomposites (Aranberri et al., 2017).

2.2 Heavy metal – car wash wastewater

Water is one of natural resources and it is very important for the living. It is crucial for to preserve the freshwater which is becoming insufficient because of the growth in population as well as the urbanisation. These continual growth cause the increasing demand of water. Presently, the crucial problems are severe contamination and inadequate water resources. Regardless of the scarcity of this valuable natural reserve, it is polluted everyday due to inappropriate effluent treatment and illegal disposal of polluted wastewater leading to public and environmental problems. This pollution caused by environmental degradation has now become a distressing problem due to rapid and unplanned urbanization, high population growth and incompetent utilisation of water reserve (Singh & Singh, 2006; Enoh & Christopher, 2015).

One of the sources of water pollution is effluent from car wash service stations. Most countries including of Malaysia were still behind in developing conscious for the wastewater produced by car wash industries (Bhatti et al., 2011). As water has becoming a rare resource in some countries, the onsite reuse and recycling of carwash wastewater are being practiced in many countries. Wastewater recycle and reuse have significantly been combined together in the professional car wash service stations. This will automatically increases the water availability and at the same time reduce pollution, preserves water resources nurtures conservation policies (Shete et al., 2014). However, there are many car wash service stations that have improper sanitation system. This will lead to improper discharge of effluent into the environment,

Cars that are washed in the street with the improper management of wastewater discharges can pollute the rivers. The surfactants, oil and grease and other pollutants that run off the car into the drains, will eventually flow to the storm water system without any treatment. Even, the measured pollutant concentrations in car wash discharge were more similar to the levels found in wastewater, than in runoff storm water (Azhari, 2010; Sablayrolles et al., 2010). The accumulated sediments during washing cars consisting concentrations of contaminants, where the sludge is considered a controlled or hazardous waste, including of metals, elevated levels of oil and grease, and unacceptable levels of acidity or alkalinity (Azhari, 2010). Malaysia have their own environmental quality regulations, but this particular regulation is seldom enforced to the car wash industry. It is generally perceived by the public that the wastewater from car washing is not severely contaminated compared with other industrial wastewaters (Lau et al., 2013). Hence, little attention is given to the car wash industry (Abagale et al., 2013).

Furthermore, the increasing use of variety of cleaning agents at the car wash stations such as synthetic detergents, engine cleaners, waxes with the combination of pollutants washed off from the vehicles have increased the potential effects of discharge from this industry (Aikins & Boakye,b 2015). Engine cleaning is notable dangerous due to the toxic components from the cleaning agents used and the high levels of oil and grease as well as heavy metals released (Aikins & Boakye,a 2015). Therefore, wastewater drained from the car wash will cause environmental problems as the pollutant such as heavy metal will continuously affect the environment. Table 2.1 indicate the heavy metal characteristics of carwash stations from several studies.

Table 2.1: Heavy metal characteristics of carwash stations from several studies

Location of sampling	Pollutant	Value (mg/l)	References
Aleppo and Latakia, Syria	Cu Zn	1.00 2.00	Baddor et al., 2014
Kumasi, Ghana	Fe Zn Cu Pb	16.69 2.07 0.26 1.14	Aikins & Boakye, 2015b
Dambovita County, Romania	Pb Cd Zn Cu	1.00 – 27.90 0.20 – 3.20 110.90 – 592.3 20.80 – 56.80	Radulescu et al., 2011
Melbourne, Australia	Cu Pb Zn	0.30 0.02 0.50	Moazzem, 2018
Zahedan, Iran	Pb Fe Zn	0.80 14.30 5.50	Bazrafshan et al., 2012
City of Tshwane, South Africa	Cr Cu Fe Mn Zn Pb Ni	0.00 – 0.03 0.00 – 0.20 0.04 – 2.29 0.10 – 0.47 0.01 – 1.96 0.01 – 0.01 0.01 – 0.04	Phungula, 2016
Gauteng Province, South Africa	Cr Cu Zn Pb	0.00 – 3.30 0.77 – 13.00 0.79 – 20.00 0.01 – 5.00	Tekere et al., 2016
Minna, Niger State, Nigeria	Mg Zn Fe Cr Cu	0.08 – 0.14 0.22 – 0.36 1.94 – 3.27 0.20 – 0.27 1.40 – 1.59	Chukwu et al., 2008
Niger Delta, Nigeria	Cu Co Ni Fe Pb Cd Cr Mn Zn	0.02 – 0.28 0.01 – 0.07 6.99 – 26.05 0.00 – 0.04 ND 0.00 – 0.02 0 – 0.03 0.21 – 1.34 0.12 – 0.53	Singru et al., 2017

**ND – not detected*

From Table 2.1, it shows that zinc, copper and iron is the common heavy metal found in the carwash wastewater with Mn can be said as rare element in carwash wastewater. Heavy metals are elements that consists of atomic weights between 63.5 and 200.6 g/mol, and a specific gravity greater than 5.0 kg/m^3. Heavy metals are more likely to accumulate in living organisms especially human as they are not biodegradable, unlike organic contaminants. These characteristics have effects on wastewater treatment system which will increase the treatment cost for particular toxic components. Despites of that, human system needs some heavy metals such as manganese, iron, chromium, copper and zinc but in the presence of large quantities of these metals, it will be toxic and extremely dangerous (Jaishankar et al., 2014).

This research focused on the removal of selected metal ions which is Zn and Mn from synthetic wastewater using chemically modified chicken feather as an adsorbent. As shown in table 2.1, the range value of concentration for both Zn and Mn are from 0.005 to 592.3 mg/l and 0.103 to 1.344 mg/l respectively.

2.3 Adsorption as the best method for heavy metal removal

Adsorption is the process which uses solid to remove substances in either from liquid or gaseous solution. Adsorption is one of the most widely used techniques for pollutant removal from contaminated mediums. The process of removing includes the process of accumulating the adsorbates and adsorbents in solutions on suitable interfaces. Adsorbates is the when substances removed from the liquid phase at the interface whereby adsorbents is the material in which can be either in the state of solid, liquid or gas phases onto which the adsorbates accumulates. Adsorption is present in many natural, physical, biological and chemical system and it is widely used. The operations utilizes solids such as activated carbon, metal hydrides, and synthetic resins. It has been widely used especially in industrial applications for the purposes of purification and treatment of both water and wastewaters.

The mechanisms, by which adsorbents remove pollutants from a solution or atmosphere, are based on a combination of physisorption and chemisorption (Kar & Misra, 2004). Physisorption refers to trapping of pollutants in a porous network or on the surface of adsorbents. Chemisorption happens at chemical functionalities present on adsorbents properties. However, the pollutant absorption depends on a range of elements such as composition of adsorbent and its amount, specific surface area and activity, physical form of adsorbent, pH of solution, initial concentration of pollutants, temperature, and also the presence of other pollutants and their concentrations.

2.3.1 Adsorption isotherm study

Adsorption equilibrium information is the most important information in understanding an adsorption process. No matter how many components are exist in the system, the adsorption equilibrium of pure components is essential for the understanding of how many those components can be accommodated by an adsorbent. It can be used in the study of adsorption kinetics of a single component, adsorption equilibrium of multicomponent systems, and then adsorption kinetics of multicomponent system.

The quantity of adsorbate that can be adsorbed by an adsorbent is a function of both characteristics and concentration of adsorbate and temperature. The characteristic of the adsorbate that are of importance includes molecular structure, solubility, molecular weight, polarity and hydrocarbon saturation. In general, the amount of adsorbate adsorbed is determined as a function of concentration at a constant temperature and a resulting function is called an adsorption isotherm. Adsorption isotherm is vital in explaining how solutes interact with adsorbents, thus optimizing the use of adsorbents. In the present study, several isotherm models have been developed to describe the process of adsorption. There are two common adsorption isotherms that are used to describe the equilibrium characteristics of adsorption which are the Langmuir and Freundlich isotherm (Rajabi et al., 2015; Mall et al., 2005).

2.3.1.1. Langmuir

Langmuir is the first isotherm theory which proposes coherent theory of adsorption onto a flat surface based on a kinetic viewpoint that is there is a continual process of bombardment of molecules onto the surface and a corresponding desorption of molecules from the surface to maintain zero rate of accumulation at the surface at equilibrium (Do, 1998). The assumptions of the Langmuir model are:

1. The surface is homogeneous, thus adsorption energy is constant over all sites
2. Adsorption on surface is localised, that is adsorbed atoms or molecules are adsorbed at definite, localised sites
3. Each site can accommodate only one atom or molecule
4. Adsorption is reversible

Langmuir theory explained that when a portion of gas molecules striking the surface, they will condense and are adhered by the surface force until these adsorbed molecules evaporate again. Figure 2.1 shows the adsorption mechanisms on a flat surface. Langmuir (1918) stated that there is proven evidence that this portion is unity, but in reality there are usually far from ideal, which makes this portion much less than unity (Do, 1998). However, on an occupied surface, when another molecule strikes the portion that are already been occupied with adsorbed species, it will evaporate very quickly, just like a reflection from a mirror.

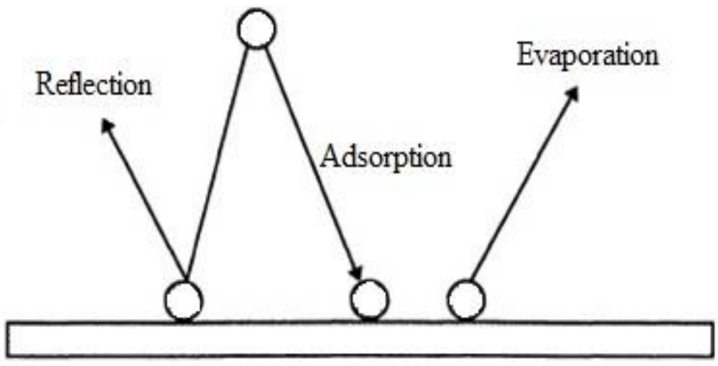

Figure 2.1 – Schematic diagram of Langmuir adsorption mechanism on a flat surface (Do, 1998)

Langmuir model is expressed by equation 2.1 below. Table 2.2 shows four types of linear form can be expressed from general Langmuir equation (Itodo et al., 2011).

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e}$$ Equation 2.1

Table 2.2 – Types of linear version derived from general Langmuir equation (Itodo et al., 2011)

Types	Equation	
1	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \left(\frac{1}{q_m}\right) C_e$	Equation 2.2
2	$\frac{1}{q} = (\frac{1}{K_L q_m}) \frac{1}{C_e} + \frac{1}{q_m}$	Equation 2.3
3	$q_e = q_m - (\frac{1}{K_L}) \frac{q_e}{C_e}$	Equation 2.4
4	$\frac{q_e}{C_e} = K_L q_m - K_L q_e$	Equation 2.5

Where:

K_L = Langmuir equilibrium constant (L/mg)

q_m = Monolayer capacity (mg/g)

q_e = Amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

C_e = Equilibrium concentration of adsorbate (mg/l)

2.3.1.2. Freundlich

Freundlich equation is one of the earliest empirical equations which used to describe the equilibrium data. This isotherm model is named to Freundlich due to the fact that it was used extensively by Freundlich even though it was also being used by many other researchers.

The description of adsorption of organics from liquid to solid phases is mostly described by using the Freundlich equation. This equation is also applicable in adsorption of gases molecules having heterogeneous surfaces, as long as the range of pressure is not too broad as this isotherm equation cannot fit into adsorption behaviour at low pressure. Furthermore, it also does not have a finite limit when pressure is sufficiently high. It is obtained by assuming that the surface is heterogeneous in the sense that the adsorption energy is distributed and the surface of topography is patch-wise, that is sites having the same adsorption energy are grouped together into one patch (Do, 1998). The adsorption energy means the interaction energy between adsorbent and adsorbate. Hence, it is generally valid in the narrow range of the adsorption data. The Freundlich equation is defined as in the Equation 2.6:

$$q_e = K_F C_e^{\frac{1}{n}}$$ Equation 2.6

Where:

q_e = Amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

K_F = Empirical Freundlich constant or capacity factor (mg/g)

C_e = Equilibrium concentration of adsorbate (mg/l)

n = Freundlich intensity parameter

1/n is an index diversity of free energies related with adsorption of the solutes by multiple components of a heterogeneous adsorbent. The isotherm is linear and the system has a constant free energy at all adsorbate concentrations when the value is 1.

A value for 1/n below 1 indicates a normal Freundlich isotherm whereby if 1/n more than 1 shows cooperative adsorption (Muherei & Junin, 2009)

2.3.2 Adsorption kinetic study

Adsorption kinetic study is the measure of the adsorption uptake with respect to time at constant pressure or concentration. The adsorption kinetic is employed to measure the diffusion of the adsorbate in the pores.

2.3.2.1. Pseudo first-order rate equation

First-order rate equation are presented by Lagergren (1898) to describe the kinetic process of liquid solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. It can be presented as follows:

$$\frac{d_{qt}}{d_t} = k_{pl}(q_e - q_t)$$ Equation 2.7

Where:

q_e = the adsorption capacities at equilibrium (mg/g)

q_t = the adsorption capacities at time (min)

k_{pl} = kinetic first order constant

By integrating Equation 2.8 with the boundary conditions of q_t=0 at t=0 and q_t=q_t at t=t, yields (Ho, 2004), it can be rearranged as follows:

$$log(q_e - q_t) = logq_e - \frac{k_{pl}}{2.303}t$$ Equation 2.8

It has been widely used in the recent years to describe the adsorption of pollutants from wastewater in various fields such as the adsorption of methylene blue from aqueous solution by broad bean peels and the removal of malachite green from aqueous solutions using oil palm trunk fibre (Hameed and El-Khaiary, 2008a; 2008b; Tan et al., 2008).

2.3.2.2. Pseudo second-order rate equation

Pseudo second order rate reaction causing the chemical reaction seems significant in the rate-controlling step and the reaction kinetics provide the best correlation of the experimental data. Moreover, the adsorption's mechanism is chemically rate controlling and because of this it is called chemisorption. In this mechanism, the kinetics of sorption should match to a reversible second order reaction at low sorbate or sorbent ratios (very low ratios at first order), and two competitive reversible second order reactions at higher sorbate/sorbent ratios.

In 1995, Ho described a kinetic process of the adsorption of divalent metal ions onto peat (Ho and McKay, 1998b),in which the chemical bonding among divalent metal ions and polar functional groups on peat, such as aldehydes, ketones, acids, and phenolics are responsible for the cation-exchange capacity of the peat. Therefore, the peat-metal reaction may be presented as shown in Equation 2.9 and 2.10, which can be dominant in the adsorption of Cu2+ ions onto peat (Coleman et al., 1956):

$$2P^{-} + Cu^{2+} \leftrightarrow CuP_2 \qquad \text{Equation 2.9}$$

$$2HP + CU^{2+} \leftrightarrow CuP_2 + 2H^{+} \qquad \text{Equation 2.10}$$

Where:

P^- and HP = active sites on the peat surface

The rate of adsorption described by Equation 2.9 and 2.10 is dependent upon the amount of divalent metal ions on the surface of peat at time t and that adsorbed at equilibrium. Therefore the rate expression may be given as:

$$\frac{d(P)_t}{d_t} = k_{p2}[(p)_0 - (p)_t]^2 \quad \text{Equation 2.11}$$

Where:

$(P)_0$ and $(HP)_0$ = the amount of equilibrium sites available on the peat

$(P)_t$ and $(HP)_t$ = the amount of active sites occupied on the peat at time t,

K_{p2} = pseudo second-order rate constant (g/(mg.min))

2.3.3 Adsorption mechanism study (Morris-Weber)

Diffusion are key process impacting the efficiency of natural attenuation. Diffusion process is necessary to accurately predict the magnitude of natural attenuation. Most of the proposed models assume that diffusion is linear and that desorption kinetics follow a first-order rate law (Angley et al., 1992; Estrella et al., 1993; Fry and Istok, 1994; Ž Brusseau et al., 1999). Only limited studies have incorporated intra-particle diffusion in the coupling of linear sorption and biodegradation (Scow and Ž Hutson, 1992; Chung et al., 1993). The morris-weber equation are as follows:

$$q_t = k_{id}t^{0.5} + C \quad \text{Equation 2.12}$$

Where:

C= the intercept related to the boundary layer effect

K_{id}= intraparticle diffusion rate constant (mg/g $min^{0.5}$)

The value of k_{id} can be evaluated from the liner slope plots of q_t versus $t^{0.5}$.

A plot of qt vs $t^{0.5}$ should be a straight line with a slope of k′ when the intra-particle diffusion is the rate-limiting step. A linear graph will give more accurate result and easier to predict the contaminant (Huang et al., 1997). This model would not be valid if adsorption kinetics is controlled by film diffusion and intra-particle diffusion simultaneously.

2.3.4 Factors affecting adsorption batch study

The adsorption batch study is affected by several aspects or operating factors such as pH, initial concentration of adsorbate, temperature and internal surface area of adsorbent which is the most important. However, initial concentration of adsorbate and the contact time are also the important factors.

2.3.4.1. Initial heavy metal concentration

The initial concentration of the adsorbate is important as it act as a driving force to overcome all mass transfer resistances of all molecules between aqueous and solid phase (Chowdhury & Saha, 2010). Therefore, a higher concentration of the adsorbate will enhance the sorption process. The higher the initial concentration of the adsorbate, the higher the adsorption efficiency (Yagub et al., 2014; Al-Asheh et al., 2003).

The adsorption is highly influenced by the heavy metal concentration of the solution, as the adsorptive reactions are directly proportional to the concentration of the solute. The initial concentration of the adsorbate provides necessary driving force to overcome the mass transfer of adsorbates between aqueous and solid phase solute. The interaction between adsorbate and adsorbent also increases when the initial concentration of the adsorbate is high. Thus, an increase in initial concentration of adsorbate will result in increase of the adsorption uptake of adsorbate (Srivastave et al., 2005).

2.3.5 Mass of adsorbent

When the adsorption process takes place on the surface of the adsorbent, the pore size on the surface is playing an important role. If the efficiency of adsorption process increase, the internal surface of the adsorbent will also increases at a given temperature (Ali et al., 2012). Therefore, the mass of the adsorbent is largely influenced by adsorption processs. The greater the initial concentration of the adsorbate, the larger the adsorption efficiency (Yagub et al., 2014; Al-Asheh et al., 2003).

The relationship between dosage of adsorbent and the removal efficiency is related to increase the number of adsorption sites and an increase in this number has no effect after equilibrium has reached (Argun et al., 2007). However, the equilibrium value of amount adsorbed is seen to decrease with an increase in the dosage.

2.3.6 Contact time

The contact time of both adsorbate and adsorbent is important in batch experiment. This is because the contact time depends on the nature of the system used. Consequently, it is important to establish the time dependence of such systems under various process conditions (Chiban et al., 2009, 2011d).

The removal of heavy metal is increased with the increasing of contact time. However, this is at the condition of a fixed heavy metal concentration with a fixed dosage of adsorbent. The study on the contact time is focusing on determining the time of the process to reach the equilibrium. Moreover, this study also is to investigate the presence of monolayer and multilayer bonds in the sorption process.

2.4 Adsorbent

There are numerous adsorbents that have been used for the adsorption of metal ions such as activated carbon, crab shell, fly ash, granular biomass, peat, modified chitosan, sewage sludge ash, peanut hulls, activated carbon cloths, zeolite, sugar beet pulp, biomaterials, kaolinite, olive stone waste, recycled alum sludge, manganese oxides, bagasse, and resins (Ihsanullah et al., 2016). However, these adsorbents deteriorate due to its low adsorption capacities or removal efficiencies of metal ions. Thus, a lot of researchers are in pursuing in exploring the new promising adsorbents.

Traditionally, there are a few of materials have been extensively studied as adsorbents in wastewater treatment. These commercial adsorbents included are silica gel, activated alumina, zeolites and activated carbon (Ihsanullah et al., 2016). However, these commercial adsorbents have some disadvantages which influence researches to investigate other alternative materials. The effectiveness of an adsorbent can be described in term of the adsorption capacity, adsorption rate as well as the possibility of regeneration (Yang, 2003). Some adsorbents proved that their effectiveness in removing a wide range of pollutants in wastewater, still, they are expensive and not practically suitable to be applied into wastewater treatment plant. Hence, the development of low cost adsorbent is supposed to enhance the future of adsorption process in wastewater treatment. The selection of the precursor for the development of low cost adsorbents depends on many factors especially freely available, inexpensive and non-hazardous in nature (Ali et al., 2012).

2.5 Chicken feather as an alternative material

The unique biomass which is the keratin protein fibre, used in removal of heavy metal from contaminated water is a promising technology. Avian keratin protein fibre is a form of animal fibrous protein, and it is extracted from the feathers of birds such as chicken and turkey (Ayutthaya et al., 2015). The effectiveness of keratin fibre in the removal of precious metals like gold is proven (Ghosh & Collie, 2014) and it is also exceptional for adsorption of iron, copper and chromium (Kumari and Sobha, 2015) from water solutions. The advantages of avian keratin fibres over other similar biosorbents is due to the abundant existence and yet cheaper bioresource compared to other similar biosorbents such as wool and silk keratin. Moreover, the properties is like high tensile strength and water insolubility, make it more attractive for biosorption (Ghosh & Collie, 2014). The production of chicken feathers is abundant and most of the feathers are disposed as waste. Consequently, the application of these keratin fibres for treatment of industrial wastewater and drinking water is very economical method and using it is equivalent to the use of one waste for clean-up of another.

2.5.1 Activation of chicken feather fibres

There are two types of activation methods that can be used to treat the chicken feather as a potential low cost adsorbent. They can be modified to improve and enhance their properties, by chemical treatment or subjected during the process of "slow pyrolysis" which is heat treatments. Activation methods prepare the chicken feather fibre with microporosity, high pore volume as well as surface area within the range of 100 to 200m^2/g. These advantages are crucial for the adsorption or separation process, purification and the storage of gases and liquids (Senoz & Wool, 2010).

2.5.1.1. Chemical Treatment

Most of the published studies with respect to the reuse of chicken feathers mainly focusing on the soluble keratin that are extracted from chicken feathers which could be reprocessed into biodegradable materials. There are a few investigations which apply raw or chemically treated chicken feathers as an adsorbent for the removal of heavy metals and dyes from effluents (Mittal et al. 2007; Chowdhury & Saha 2012).

The chemical treatment is used to improve the chicken feather fibre as a potential low cost adsorbent by modifying the keratin structures as well as adding some functional groups to increase the selectivity and be more effective in adsorption process. In order to remove the existing organic materials that present in the chicken feathers, they are treated with either acidic or alkaline treatment process to make it dissolve and break the keratin structure as well as the binding organic materials. The product is then washed with distilled water and dried in the oven for days. Table 2.3 shows some research in activating the chicken feathers as adsorbents.

Table 2.3 – Examples of preparation of chicken feather by chemical treatment process

Type of chemical activation	Steps/reagent used	Heavy metal/pollutant	References
Acidic treatment	Hydrogen peroxide	Indigo Carmine	Mittal et al., 2007a
Acidic treatment	Aqueous tannic acid solution	Pb ions	Kumari et al., 2011
Acidic treatment	1) The feathers were treated with aqueous acetic acid and neutralized with sodium bicarbonate ($NaHCO_3$). 2) Chitosan was dissolved in aqueous acetic acid. 3) The neutralized treated feathers solution were added into the chitosan solution. 4) The mixture was dropped into an alkaline coagulant solution.	Cu ions	Kumari and Sobha, 2015
Alkaline treatment	Sodium dodecylbenzene sulphonate and 1-butyl-3-methylimidazolium chloride. The preparation is modified by method of Huddleston et al., 2001	Cr (IV) ions	Sun et al., 2009
Alkaline treatment	Several factors being considered in the adsorbent preparation: 1) Dosage of sodium bisulphite ($NaHSO_3$) 2) Dosage of urea 3) Dosage of sodium dodecyl sulphate (SDS) This three dosage added depends on the CF dosage	Analytical grade methylene blue	Gao et al., 2014
Acidic and alkaline treatment	Two types of adsorbent: 1) Keratin agent (KA) – the feathers were treated first with hydrochloric acid and then with sodium bisulphite solution and finally hydrolyzed with sodium hydroxide solution. The liquid extract from the last step of poultry keratin is designated as KA. 2) Composite – Mixing the KA with dye fixing agent in a rotary reactor	Acid blue – A dye	Chen et al., 2016

In this study, the alkaline treatment using NaOH solution has been reacted to the functional group in the amino acid of the keratin. Therefore, the usage of Epichlorohydrin as cross-linking reagent to form covalent bond with the carbon atoms linked to the hydroxyl groups in the hydrolysate (Su et al., 2016; Galhoum et al., 2015; Ping et al., 2009). This result in the rupturing of the epoxide ring and the release of a chlorine atom.

The last modification step is by using Ethylenediamine reagent as a purpose of adding some functional group into the surface of the chicken feather (Su et al., 2016; Ping et al., 2009). Ethylenediamine is a chelating agent which is commonly used to isolate metal ions due to its role as a hexadentate ligand, which is the combination of two amines and four carboxylate groups (Su et al., 2016). In this step, the cross-linking reagent reacts with peptide backbone of the keratin which resulted in opening of epoxide ring thus directly reacts with amino groups from the chelating agent (Galhoum et al., 2015). After the cross-linking process, the chloride-ends from the reaction of cross-linking process are stayed available which will be reacted with the amino group in the chelating agent with the releasing of the chlorine (Galhoum et al., 2015).

2.5.1.2. Physical treatment

Pyrolysis process is an irreversible reaction which occurs via thermal treatment in the absence of oxygen with flow on nitrogen gas (Kardas et al., 2015). During carbonization, pyrolytic decomposition of precursor occurs together with the concurrent elimination of many noncarbon species (H, N, O and S). This process is where low molecular weight volatiles are inititally released and then followed by light aromatics and finally, hydrogen gas. The resultant product gained is in the form of a fixed carbonaceous char (Kluska et al., 2016). The pores formed during carbonization are filled with tarry pyrolysis residues and it requires activation in order to develop the internal