ACTIVATED CARBON, LIMESTONE AND ALGINATE AS A COMPOSITE ADSORBENT FOR RIVER WATER TREATMENT

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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

Pencemaran air telah menjadi satu masalah yang serius kepada alam sekitar dan kesihatan manusia. Ia boleh menjejaskan badan manusia jika air yang tercemar kerap digunakan. Oleh itu, rawatan air sisa telah diberikan perhatian baru-baru ini dengan proses penjerapan menggunakan adsorben kos rendah. Dalam kajian ini, proses penjerapan telah diiktiraf sebagai salah satu proses yang mempunyai kelebihan dari segi kos permulaan yang rendah, kemudahan operasi dan reka bentuk mudah. Permohonan penjerap komposit seperti gabungan karbon diaktifkan, batu kapur, alginate sebagai pengikat dan kemolaran kalsium klorida dehidrasi telah dijalankan untuk menilai kesesuaian media komposit untuk digunakan untuk rawatan air sisa. Dua nisbah bahan penjerap yang digubah telah disediakan sebagai media untuk mengeluarkan kekeruhan dan warna dalam air sisa. Nisbah yang telah disediakan adalah AC (3): LS (7): AG (2) dan AC (5): LS (5): AG (2). Selepas campuran adsorben disediakan, satu kajian kelompok awal telah dijalankan untuk memilih keadaan optimum untuk faktor-faktor bagi setiap nisbah. Faktor-faktor yang telah diuji adalah dos bahan penjerap, masa sentuhan, kelajuan goncangan dan masa penetapan. Selepas diperolehi keadaan optimum untuk faktor, kedua-dua nisbah telah diuji untuk memilih nisbah terbaik penjerap. Hasil kajian menunjukkan bahawa keadaan optimum untuk faktor-faktor untuk nisbah 3: 7: 2 adalah 9 gram dos bahan penjerap, 60 minit masa sentuhan, 150 rpm kelajuan goncangan dan 60 minit masa penurunan. Sementara itu, keadaan optimum untuk nisbah 5: 5: 2 adalah 13 gram dos bahan penjerap, 80 minit masa sentuhan, 150 rpm kelajuan goncangan dan 60 minit masa penurunan. Keputusan untuk membandingkan kedua-dua nisbah menunjukkan bahawa nisbah 5: 5: 2 mempunyai penyingkiran peratusan yang lebih tinggi kekeruhan dan warna daripada nisbah 3: 7: 2 dari segi faktor yang dipilih.

ABSTRACT

Water contamination has been a serious problem to the environment and human health. It can adversely affect the human body if contaminated water is consumed regularly. Thus, wastewater treatment has been given much attention recently by the adsorption process using the low cost adsorbents. In this study, adsorption process has been recognized as one of the process that had advantages in terms of low starting cost, ease of operation and simplified design. The application of composite adsorbent such as a combination of activated carbon, limestone, alginate as a binder and molarity of calcium chloride dehydrated was carried out to assess the suitability of composite media to be applied for wastewater treatment. Two ratios of the composite adsorbent had been prepared as the media for removing turbidity and colour in wastewater. The ratios that had been prepared were AC (3): LS (7): AG (2) and AC (5): LS (5): AG (2). After prepared the composited adsorbent, a preliminary batch studies were carry out to choose the optimum conditions for the factors of every ratio. The factors that had been tested were dosages of adsorbent, contact time, shaking speed and settling time. After obtaining the optimum condition for the factors, both ratios had been tested to choose the best ratio for the adsorbent. Results showed that the optimum conditions for the factors for the ratio 3:7:2 were 9 grams of dosages of the adsorbent, 60 minutes of the contact time, 150 rpm of the shaking speed and 60 minutes of the settling time. Meanwhile, the optimum condition for the ratio 5:5:2 were 13 grams dosages of the adsorbent, 80 minutes of the contact time, 150 rpm of the shaking speed and 60 minutes of the settling time. The results for comparing both ratios showed that the ratio 5:5:2 had the higher percentage removal of turbidity and colour than ratio 3:7:2 in terms of the selecting factors.

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LIST OF ABBREVIATIONS

AC	**A**ctivated **C**arbon
LS	**L**imestone
AG	**A**lginate
WHO	**W**orld **H**ealth **O**rganization
RO	**R**everse **O**smosis
GAC	**G**ranular **A**ctivated **C**arbon
PAC	**P**owdered **A**ctivated **C**arbon
WTP	**W**ater **T**reatment **P**lant
MBR	**M**embrane **B**io **R**eactor

NOMENCLATURES

C_e	Equilibrium concentration of the adsorbate
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent
Q_o	Maximum monolayer adsorption capacity of the adsorbent
K_L	Langmuir adsorption constant with respect to the free energy adsorption
K_F	Freundlich constant
n	Freundlich heterogeneity factor
W_i	Initial color concentration
W_f	Final color concentration
T_i	Initial turbidity concentration
T_f	Final turbidity concentration
k_1	Rate constant of pseudo-first order sorption
k_2	Rate constant of pseudo-second order sorption

CHAPTER 1

INTRODUCTION

1.1 Background

Nature has provided plenty of resources that are used to sustain and develop life on this planet. One of the most important resources that available to us is water. The distribution of water on the Earth's surface is extremely uneven. Only 3% of water on the surface is fresh while the remaining 97% resides in the ocean (Matt Williams, 2016). From the freshwater, 69% resides in glaciers, 30% underground, and less than 1% is located in lakes, rivers and swamps (Dana Desonie, 2016). Looked at another way, only one percent of the water on the Earth's surface is usable by humans and 99% of the usable quantity is situated underground (Drs. Timothy Bralower and David Bice, n.d.). Thus, the amount of usable water is very limited and this resource very important to environment and human health. The rapid growth of population leads to the growing demand of water usage for drinking, irrigation, municipal and industrial development (Afroz et al., 2014).

Rapid changes in agricultural and industrial activities have undermined the quality of river water. One of the major sources of water pollution is industrial wastewater that brings harm to human health as well as aquatic organism like fishes. Aquatic life like fishes will expose to danger in that polluted river (Ali et al., 2011). In urban areas, the disposal from industrial may contribute greatly to the contamination of the water (Chaurasia et al., 2011). These contaminants include organic and inorganic chemicals. Therefore, treatment of water is required to remove those contaminants before consumption (Crittenden et al., 2012).

Due to the acidity and high concentration of organic material causes many problems to the water and the water treatment process including negative effect on water quality that caused by colour, taste and odor problems and increases of coagulant (Matilainen et al., 2010). Selective treatment and purification for river water must be conducted prior to be used as water supply and demand. Several methods for water purification have been applied such as distillation, adsorption, flocculation, coagulation and others. By consider the most suitable methods to be chosen are important and it can save the cost effectively for the water treatment process.

Currently, in some developed countries, water is treated through the process of flocculation and chlorination disinfection processes. Unfortunately, these processes cannot treat the organic matter effectively. After chlorination, disinfection by products are formed when attacked by chlorine radical disinfection (Crittenden et al., 2012). Besides chlorination disinfection process, adsorption process also has used in some countries. Adsorption process has been known as one the simple and effective technique for water treatment and this technique greatly depends on the development of an efficient adsorbent for effective treatment (Faust and Aly, 2013).

1.2 Problem Statement

Water is very important to the environment and human which safe, adequate and accessible supply must be available to all (Wang and Peng, 2012). Improving access to safe drinking-water can result in benefits to better quality health. Every effort should be made to achieve drinking-water that is as safe as practicable (World Health Organization, 2011). Maintain and secure the clean water supply has been one of the vital factors nowadays. The increasing number of populations however has gives more pressure on limited high-quality surface sources. Contamination of water with municipal, agricultural, and industrial wastes has led to a deterioration of water quality in many other sources. Thus, the quality of the water source cannot be ovelooked in water supply development. This means, more sources of water require some treatment before able to be used (Howe et al., 2012) .

In many developing countries, access to clean and safe water is a big issue. Because of diarrhea which is caused by polluted water, more than six million people die. Developing countries pay a high cost to import chemicals for water treatment (Asrafuzzaman et al., 2011). The high turbidity in surface water has make it difficult for water treatment plants to supply the drinking water (Hu et al., 2013). Therefore, the water must be treated first before being used for drinking. Various methods have been used to make water clean and safe to the consumer. The treatment method that being used was depend on the character of the raw water. One of the problems with treatment of surface water is the large seasonal variation in turbidity (Asrafuzzaman et al., 2011).

Adsorption process is considered to be a superior option because of its convenience, ease of operation and simplicity of design. Adsorption studies have been conducted in removing turbidity and colour from river water (Syafalni et al., 2012). In adsorption, it is good to distinguish between physical adsorption, that involve only relatively weak intermolecular forces which involves the formation of a chemical bond between the molecule and the surface of the adsorbent. Adsorption has been found to be preferable and advantageous to other techniques in terms of initial cost, flexibility, and simplicity of design ease operation (Chunjie Li et al., 2011).

Although the adsorption technique is versatile and is easy to adopt in practical forms, the adsorbent materials like activated carbon is costly. Hence development of a suitable composite media that shows a high adsorption capacity at low cost is a promising route for selectively remove contaminants from water (Iram et al., 2010). As mentioned before, activated carbon is one of the adsorbents that are widely used for adsorption process in water treatment (Wang and Peng, 2010). However, activated carbon is considerably expensive material which the greater the quality of activated carbon, the higher the cost (Ghaedi et al., 2012). Due to this problem, many researches have been carry out to produce alternative adsorbents to replace the costly activated carbon. The purpose is to produce various adsorbents which able to remove contaminants for water treatment at lower cost.

Thus, the purpose of this study is to develop new composite adsorbent for river water treatment to determine the efficiency of new composite media for removal the colour and turbidity. The composite media consist of activated carbon, limestone and alginate. There were two ratios that had been tested in this experiment. The two ratios that were tested in this study AC (3): LS (7): AG (2) and AC (5): LS (5): AG (2). This study focused on the treatment of Kerian River Water at Lubuk Buntar. It is located at Bandar Baharu, Kedah with at 5°08'14.1"N and 100°35'09.8"E. This river has a potential to be used as a water intake area.

1.3 Objectives

This research is conducted principally to treat the river water. Water collected from Kerian River at Lubuk Buntar is treated with several adsorbents consisting of activated carbon, limestone and alginate. Therefore, this research will include the objectives as follows:

1. To determine the best ratio of new composite adsorbent, consist of activated carbon, limestone, and alginate for river water treatment.
2. To select the most significance factor of new composite adsorbent for removal of colour and turbidity.

1.4 Dissertation Outline

This thesis contains five main chapters where every chapter explains different parts of this study.

Chapter 1 **Introduction.** A brief introduction of the research work, background study, problem statement, gap of knowledge and objectives of research.

Chapter 2 **Literature review.** A comprehensive review of literature according to this research. In this chapter, the pollutants in surface water, turbidity and colour in water will be elaborated. Further information about treatment of surface water and adsorbent that are being used will be described. Adsorption isotherm and kinetics also are presented in this chapter.

Chapter 3 **Methodology.** This chapter presents research methodology that is conducted to accomplish the research's objectives. Besides, site location, sampling procedures, materials used and properties as well as composite adsorbent preparations are presented in this chapter.

Chatper 4 **Results and Discussions.** This chapter will discuss the results and data of the experiments. Discussion will be presented with the aid of tables and graph.

Chapter 5 **Conclusions and Recommendations**. The conclusions and recommendations based on the findings are discussed and future work prospects are elaborated.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Surface water and groundwater can be contaminated from many sources which could cause risk to human health. Rain fall that flow on the surface of grounds is drained into the rivers and streams. When the water flow on the grounds, various contaminants are disposed faster than standing water. These problems are very danger as it can cause a negative impact on water sustainability other than the environment and human health. There are many reasons that water pollution can happen. One of the reasons is urbanization. Urbanization can cause water pollution due to high population and human activities. It alters the quality of river catchments which deteriorates the quality of receiving water distributed to domestic and industrial areas (Afroz et al., 2014). As water runs on the ground surface, it may collect various contaminants including organic and inorganic compounds, animal wastes, and soil particles together (Howe et al., 2012). Therefore, treatment of water is required to remove those contaminants (Crittenden et al., 2012). There are a lot of methods that have been used in water treatment. However, adsorption process has been widely used in many countries due to its inexpensiveness and ease of operation (Fu and Wang, 2011). This chapter will include about the adsorption, kinetic and adsorption isotherms. The pollutants that contain in surface water and treatment for the surface water will be discussed in this chapter. This chapter also provides a review on the properties of activated carbon, limestone and alginate as the composite adsorbent.

2.2 Pollutants in surface water

Water is classified as surface water when any natural water that collects on the surface of the earth and not penetrated much below of the surface of the ground (Merriam-Webster). This includes oceans, seas, lakes, rivers or wetlands. Fresh surface water is maintained by rainfall or other precipitation and it is lost through the seepage in the ground, evaporation or use by plants and animals. There are many essential properties of surface water such as temperature, saltiness or salinity, turbidity, and levels of dissolved nutrients, such as oxygen and carbon dioxide (David Wood, n.d.). Due to the surface water directly exposed to the open air (atmosphere) that will regulate the oxidization process, it may contain various contaminants (James, 2011).

The presence of organic and inorganic contaminants in surface water has posed to be one of the pervasive enviromental issues (Moore and J.W. et al., 2012). These pollutants can be hazardous to human, animals and plants (Wang et al., 2010). The reason for this is that all three major sources of pollution like industry, agriculture and domestic are concentrated along the rivers. One of the evidence that agriculture can cause pollution to river is farmers use fertilizers and pesticides on their crops to make them grow better. The main problem is if the amounts of fertilizers or farm waste drain into a river too huge, the concentration of nitrate and phosphate in the water increases considerably. Algae will use these substances to grow and multiply rapidly. This massive growth of algae, called eutrophication can lead to river water pollution (Lenntech BV, n.d.). Besides that, agricultural also can raise the concentrations of pollutants such as chloride or total suspended solids in the surface waters and cause high turbidity and colour (Omstead et al., 2013).

2.21 Turbidity

Turbidity is a general term used to describe the optical opacity of water containing any form insoluble matter or suspended solids that are freely suspended in water. In other word, turbidity is a measure of the clarity of water to the eye. The water can be classified particularly clear when the concentration of the turbidity is low. High level of turbidity concentration if river water, can reduce the amount of light reaching deep to the bottom of the river water (The USGS Water Science School, 2016). Hence, it can reduce the growth of plants and effect the other species such as fishes that eat plants. Besides that, it will make some fishes hard to absorb oxygen.

Turbidity is one of the important aesthetic properties of potable water and it is also very useful in defining drinking water quality. Turbidity can impact a huge problem in water treatment (Asrafuzzaman et al., 2011). If the turbidity in the water is too high, the water cannot be used for drinking. A lack of water supply can cause a huge problem to environment and human (Hu et al., 2013). In open water, organisms like phytoplankton can contribute to turbidity. Erosion and effluent from highly urbanized zones contribute to the turbidity of waters in those areas. Construction, mining and agriculture may disturb the soil and can lead to an increase levels of sediment which run off into waterways during storms (La Motte Company, 2017). Turbidity and colour that produced by finely dispersed suspended and colloidal particles cannot be removed sufficiently except through water treatment (Ali et al., 2010).

2.22 Colour

Colour is one of the most fundamental water qualities to be monitored. Colour is a property of natural and conducted water what is perceivable to most people without any kind of instrumentations. Water takes on colour as the result of organic matter from decaying vegetation. Colour is commonly a problem of only surface water. Colour is also a result of the presence of metals like iron and manganese. Every colour in water indicates the matter that contain in it such as reddish brown colour indicates the presence of iron which will precipitate when the water is exposed to air (Massachusetts Dept. of Environmental Protection, n.d.).

Colour in water can be formed by a number of contaminants such as iron which changes in the presence of oxygen to red sediment. Colour in water is not a toxic characteristic, but it can affect the appearance and palatability of the water (Mr. Brian Oram, n.d.). Colour in water is usually associated with aromatic compounds that produced from the decay of natural herbal substances (Malakootian and Fatehizadeh, 2010). Although colour is not a toxic characteristic in water, but it can cause a big problem to aquatic plant and other species in water. Highly concentrations of color in river water has significant effects on aquatic plants and other species like fishes. Light is very critical for the growth of aquatic plants and high concentration of color in water can limit the penetration of light. Thus, a highly coloured in water could not sustain aquatic life which could lead to the long-term impairment of the ecosystem (The USGS Water Science School, 2016).

Colour is one of the big issues in river water and many techniques can be applied to remove it. One of the techniques is through coagulation and flocculation process (Riera-Torres, 2010). Another treatment that can be used for removal of colour in water is by activated carbon. When the capacity of the activated carbon for the adsorption of the color exhausted, it must be replaced (Mr. Brian Oram, n.d.). A standard scale has been developed for measuring colour intensity in water. When the scale of colour in water is 5 units, it means that the colour of this water is equal in intensity to the colour of distilled water containing 5 milligrams of platinum as potassium chloroplatinate per litre (APEC water).

2.3 Treatment of surface water

Rivers are the most important freshwater resource and one of the sources of surface water. River water is contaminated by physical impurities consist of totals suspended solids, turbidity, bacteria and other contaminants which need to be removed before supply and distribution of river water for various uses. River water treatment is the process of removing contaminants from flowing which includes physio-chemical treatment of water with the combination of conventional and advance treatment process like coagulation, flocculation, clarification, settling, filtration and disinfection of filter water to produce an environmentally safe and pure water which is suitable for drinking and multiple uses (Shubham).

The process of selection of a suitable treatment system is based on the constituents' properties in water and the ability of the process to exploit the differences of the constituents' properties. For example, adsorption depends on the difference in polarity and hydrophobicity between a constituent and water. The more nonpolar a compound is, the stronger it absorbs onto a nonpolar adsorbent like activated carbon (AC) (Howe et al., 2012).

Various methods of water treatment such as membrane filtration, ion exchange, reverse osmosis, advanced oxidation processes, coagulation and flocculation do not seem to be economically feasible. For instance, membrane filtration tends to increase the cost of its operation due to the membrane fouling (Mohammed et al., 2014). For ion exchange, reverse osmosis and advance oxidation processes are economically unfeasible because of their high operating utility and cost (Rashed, 2013).

Membrane filtration processes is one of the technique to treat surface water and produce an environmentally safe and pure water which is suitable for drinking and multiple uses. This method shows irreplaceable advantages, such as low energy cost which is mainly for pumping, low capital investment, little chemicals requirements that only for membrane cleaning, relative uncritical scale-up and high throughput while maintaining product purity under ambient conditions. However, one of the major problems of this method is membrane fouling which is defined as the drop in the membrane flux with time (Acero et al., 2010). Membrane fouling is one of the big issue in membrane filtration processes and it is a major factor in determining their practical application in water treatment and desalination in terms of technology and economics (Nguyen et al., 2012).

Coagulation-flocculation treatment process has been found to be easy to operate and energy saving treatment. Several studies have been reported on the performance and optimization of coagulants, determination of pH and investigation of flocculants addition (Solanki et al., 2013). However, a major disadvantage of this technique is the operational costs relatively high. To achieve the effective level of flocculation, desired quantities of coagulant and flocculant are needed and accurate. A certain quantity of physico-chemical sludge is also formed, which is normally processed externally (Emis, 2010a).

Reverse osmosis (RO) is water treatment process of membrane technology that widely used in the production of potable water. This technology can reduce various organic contamination such as the chemical oxygen demand (COD) and the Total Organic Carbon (TOC). One of the advantages of this technique is that it has membrane processes such as modular construction and small footprint which allow the combination with other treatment processes. The technology employs semi-permeable membranes that allow to separate a solution into two streams which are permeate, containing the purified water that passes through the membrane, and concentrate the portion that contains salts and retained compounds. Therefore, it needs a suitable and environmentally friendly management option (Pérez-González et al., 2012). This technology efficiency is depending on the operational parameters and on membrane and feed water properties (Malaeb and Ayoub, 2011).

Adsorption is one of the physicochemical treatment processes and found to be the most ideal technique in water treatment as it is simple, ease to operate and there is a vast selection of adsorbents available such as activated carbon (Kamaruddin et al., 2013).

2.4 Adsorption

Adsorption is a water treatment technique for removing many compounds from water. Adsorption is most commonly implemented for the removal of low concentrations of non-degradable organic compounds from river water, drinking water preparation, and process water. Adsorption process takes place when molecules in a liquid bind themselves to the surface of a solid substance (Emis 2010b). Adsorption also can be classified as a surface phenomenon that is the increase in concentration of a particular component at the surface or interfere between two phases. In any solid or liquid state, atoms at the surface are tends to unbalance forces of attraction to the surface plane. These forces are merely extensions of the force acting within the body of the material and are ultimately responsible for the phenomenon of adsorption (Faust and Aly, 2013).

Adsorption process can be classified as a superior option because of its convenience, ease of operation and simplicity of design. Adsorption studies have been conducted in removing turbidity and colour from river water (Syafalni et al., 2012). In this process, it is good to distinguish between physical adsorption which involve only relatively weak intermolecular forces. This intermolecular force involves the formation of a chemical bond between the molecule and the surface of the adsorbent. Adsorption has been found to be preferable and advantageous to other techniques in terms of initial cost, flexibility, and simplicity of design and ease of operation (Chunjie Li et al., 2011).

2.4.1 Mechanism of Adsorption

The term adsorption can be described by two kinds of adsorption mechanisms. The mechanisms are chemisorption (chemical adsorption) and physisorption (physical adsorption). Chemisorption is a type of adsorption whereby the attraction between the adsorbent and adsorbate through the formation of a chemical bond with shorter bond length, resulting in releasing energy which is known as exothermic process. This type of adsorption involves high adsorption energy which is higher than 1 eV per adsorbent molecule. Therefore, desorption is impossible or may need high amount of energy to reverse the process for recycling the adsorbent. As for physisorption, it is the second type of adsorption whereby the attraction between the adsorbent and adsorbate through the Van der Waals interactions. Physisorption is industrially favoured due to the low adsorption energy which is lower than 1 eV per adsorbent molecule, thus requiring shorter time than that of the chemisorption. In addition, the simplicity of desorption process will be enhanced. Besides that, the adsorption on low cost adsorbent is usually controlled by physical forces include Van Der Waals forces, hydrophobicity, hydrogen bonds, polarity and steric interaction, dipole interaction and others (Ali et al., 2012). The differences of physisorption and chemisorption are summarized in Table 2.1 below (Atkins and De Paula, 2011).

Table 2.1: Properties of physisorption and chemisorption

Physisorption	**Chemisorption**
• Multilayer adsorption	• Monolayer
• Low degree of specificity	• Depends on the reactivity of adsorbent and adsorbate substance
• Desorption is possible as adsorbed molecule keep its identity	• Desorption is impossible as adsorbed molecule loses its identity
• Exothermic	• Exothermic or endothermic
• System generally reaches thermodynamic equilibrium rapidly	• Activation energy is involved and system may not reach equilibrium

2.4.2 Adsorption Isotherm

Adsorption isotherm is an invaluable curve that describe the phenomenon governing the retention or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature. In other words, it is the graph between the amounts of adsorbate absorbed (x) and the concentration of the adsorbate in the fluid phase (m) at constant temperature. In the process of adsorption, adsorbate gets adsorbed on adsorbent. For the adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration (Foo and Hameed, 2010). Based on Le-Chatelier principle, the direction of equilibrium would shift in the direction where the stress can be relieved. In case of application of excess pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored (Chemistry Learning, 2009).

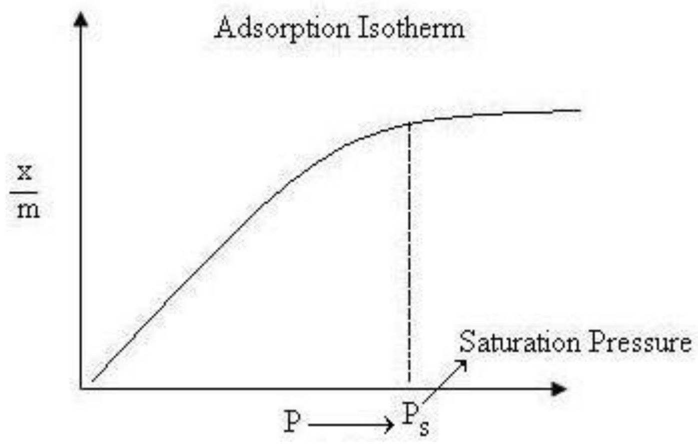

Figure 2.1: Basic Adsorption Isotherm

Figure 2.1 shows that we can predict the adsorption equilibrium after saturation pressure (Ps) adsorption does not occur anymore. This can be explained that there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process (Chemistry Learning, 2009a).

2.4.2.1 Langmuir Isotherm

The Langmuir isotherm was developed on the assumption that the adsorption process occurs at specific homogeneous sites within the adsorbent surface with uniform distribution of energy level. Basically, once the adsorbate is attached on the site, no further adsorption can take place at that site which concludes that the adsorption process is monolayer in nature. The Langmuir isotherm can be described based on these assumptions (Chemistry Learning, 2009b):

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.
5. Adsorption is monolayer or unilayer.

Langmuir model is based on the assumption of a homogeneous adsorbent surface with identical adsorption sites which can be expressed by the following equation (Liu et al., 2010):

$$q_e = \frac{Q_o K_L C_e}{1+K_L C_e} \quad (2.1)$$

The linear form of Langmuir isotherm equation is given by Equation 2.2.

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \quad (2.2)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_o is the maximum monolayer adsorption capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant with respect to the free energy adsorption (L/mg). The constant value can be evaluated from the intercept and the slope of the linear plot of the experimental data, (C_e/q_e) against C_e.

2.4.2.2 Freundlich Isotherm

Freundlich isotherm assumption can be defined as the adsorption occurs on heterogenous surfaces with different energy of adsorption. Freundlich model equation can be expressed in the following equation (Jeppu and Clement, 2012).

$$q_e = K_F C_e^{1/n} \qquad (2.3)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), K_F is the Freundlich constant $(mg/g)(L/mg)^{1/n}$ and n is the Freundlich heterogeneity factor. The equation can be used in linear form by taking the logarithmic of both sides as shown in Equation 2.4 (Ecetoc):

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad (2.4)$$

Briefly, a plot of ($\log q_e$) against ($\log C_e$) yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constant can be obtained from the slope and intercept of the linear plot of experimental data. The value of n indicates favourable adsorption when $1<n<10$.

2.4.3 Adsorption Kinetics

The objective of this research is to investigate the adsorption kinetics of turbidity and color removal by composite adsorbent at varying contact time. Sorption kinetics is investigated to develop an understanding of controlling reaction pathways (e.g., chemisorption versus physisorption) and the mechanisms of sorption reactions (Boparai et al., 2011). The adsorption kinetics is important for adsorption studies because it can predict the rate at which a pollutant is removed from aqueous solutions and provides valuable data for understanding the mechanism of sorption reactions and equilibrium adsorption isotherms are used to quantify the adsorptive capacity of an adsorbent (Cheng et al., 2011). Among kinetic models, the pseudo-first-order and pseudo-second-order are commonly used in adsorbent-adsorbate system.

The pseudo-first-order kinetic model equation of Largergren is generally expressed as follows:

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \quad (2.5)$$

where q_e is the amount of adsorbate adsorbed at equilibrium, (mg/g), q_t is the amount of solute adsorb per unit weight of adsorbent at time, (mg/g), k_1 is the rate constant of pseudo-first order sorption (1/h). Integrating Equation (2.5) for the boundary conditions t = 0 to t and q_t=0 to q_t, gives the following equation:

$$\log(q_e - q_t) = \log q_e + \left(\frac{k_1}{2.303}\right)t \quad (2.6)$$

The pseudo-second-order equations predict the behaviour over the whole range of adsorption and it is in agreement with the adsorption mechanism being the rate controlling step. The pseudo-second-order equations that are based on equilibrium adsorption can be expressed as:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \quad (2.7)$$

where q_e is the amount of adsorbate adsorbed at equilibrium, (mg/g), q_t is the amount of solute adsorbed per unit weight of adsorbent at time, t (mg/g), k_2 is the rate constant of pseudo-second-order sorption (g/h.mg). Integrating Equation 2.7 for the boundary conditions t = 0 to t and q_t = 0 to q_t, gives the following equation:

$$\frac{1}{q_e - q_t} = \frac{1}{q_{e_2}} + k_2 t \tag{2.8}$$

which is integrated rate low for a pseudo-second-order reaction. Equation 2.8 can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2.9}$$

The linear plot of t/q_e versus t gives $1/q_e$ the slope and $1/k_2q_e^2$ as the intercept.

2.4.4 Factors Affecting Adsorption Process

The adsorption process is affected by several factors such as dosage of adsorbent, shaking speed, contact time, settling time and others factor (Faust and Aly, 2013). One of the factors that affect the adsorption process is the dosage of the adsorbent. The removal efficiency increases as the adsorbent dosage increases until saturation point is achieved. The equilibrium concentration decreases with increasing adsorbent dosage for a given initial pollutants concentration because for a fixed initial solute concentration, increasing adsorbent doses provide greater surface area or adsorption sites (Faust and Aly, 1998). Besides that, increasing in dosage of adsorbent will produce more active sites which become available for the adsorbent uptake (Anwar et al., 2010).

Besides dosage of adsorbent, performance of adsorption capacity also depends on the contact time of the process. Contact time influences the rate of adsorption via exchangers and the removal efficiency increases with increase in time (Iram et al., 2010). According to Zheng et al. (2010), The concentration of contaminants in the aqueous solution decreased gradually with increasing the contact time until the maximum sorption of the adsorbent was achieved. The initial rapid removal of contaminants from aqueous solution may be attributed to the highly hydrophobic surface of adsorbent which may preferentially sorb hydrophobic solutes from water. However, the surface of the adsorbent would be hydrated once contacting with water which would alter its hydrophobic property.

Shaking speed is also one of the factors that can affect the efficiency of adsorption capacity. According to the research that had been conducted by Albadarin et al. (2012), the adsorbate ions that spread in the aqueous solution is affected by shaking speed. The effect of the shaking speeds (100, 150 and 200 rpm) on the adsorption of contaminants onto composite adsorbent had been conducted. The rate of shaking has a clear effect on the amount of pollutant uptake which may indicate that mass transfer is a key factor in controlling the rate. The amount of pollutants adsorbed increased from 10.05 to 10.67 mg/g when the rate of shaking increased from 100 rpm to 200 rpm. This can be attributed to the increase of the mobility of the system and decrease in the film resistance to mass transfer surrounding the adsorbent particle. According to Dotto and Pinto (2011), the stirring rates from 100 to 200 are in the average range of agitations rates, and usually in this range a slight change in adsorption behaviour takes place.

Another factor that can affect the adsorption performance is settling time. In the adsorption process, the settling time is an important factor which can influence the overall removal efficiencies of contaminants in surface water treatment (Thirugnanasambandham et al., 2013). Settling time can give an impact in simulated sedimentation after shaking of the adsorbent mixtures on sorption capacity. The longer the settling time, the higher the removal efficiency of contaminants in adsorption process (Hussain et al., 2011).

2.5 Adsorbent

In recent years, various adsorbents of interest in water treatment are studied include activated carbon, ion exchange resins, hydroxides, activated alumina, clays, zeolites and other solids that are suspended in or in contact with water (James, 2011). The effectiveness of an adsorbent is predicted based on its capacity, adsorption rate, its mechanical strength, possibility of regeneration and reuse. Although some of them are found effectively in removing a wide range of pollutants in water, they are expensive and not advisable to use at large scale.

One of the example is activated carbon. Activated carbon is the most widely used adsorbent for water treatment due to its characteristics such as high surface area (ranges from 500 to 1500 m2 g^{-1}), well-developed internal micro porosity and wide spectrum surface functional groups (Rivera-Utrilla et al., 2011) play an important role in the adsorption, as they determine the interactions between the organics and the activated carbon at the interface (Liu et al., 2010). However, this technology is economically not efficient due to the manufacture of activated carbon is complex and expensive. Therefore, the development of low cost adsorbent is believed in boosting the bright future of adsorption process. The selection of the precursor for the development of low cost adsorbents depends upon many factors especially freely available, inexpensive and non-hazardous in nature (Ali et al., 2012).

2.5.1 Activated Carbon

Activated carbon has been proven to be an ideal adsorbent for the removal of a wide range of organic and inorganic pollutants for water treatment. Commercial activated carbon is usually derived from biomass, lignite (lignocellulosic materials) or coal. In fact, any carbonaceous materials can be used as precursors for the preparation of carbon-based adsorbents because of their availability and cheapness (Rafatullah et al., 2010).

Besides that, activated carbon provides an attachment wide surface for micro-organisms to bio regenerate the activated carbon. Combinations of organic and inorganic pollutants that presence in water need adsorbents which have the ability to remove a variety of pollutants including organic and inorganic species. It is well known that activated carbons are the most effective adsorbents for the removal of organic pollutants from the aqueous solution. Therefore, this type of adsorbent is widely applied as a commercial adsorbent in the purification of water (Halim et al., 2010).

There are many types of activated carbon that are being used in water treatment. One of the activated carbon types is granular activated carbon (GAC). Granular activated carbon is produced from hard materials that may be used to remove pollutants from wastewater with no requirement to separate the activated carbon from bulk fluid. Large particle size of GAC presents a smaller surface area thus suitable for diffusion (gas and odour) purpose. Another type of activated carbon is powdered activated carbon (PAC). PAC may be obtained from crushed ground carbon particles that pass designated sieve aperture. Typical size of PAC granules is less than 1.0 mm with average diameters of 0.15 to 0.25 mm (Salleh et al., 2011).

The application of activated carbon in adsorption process is mainly depends on the surface chemistry and pore structure of porous carbons. The method of activation and the nature of precursor used greatly influences surface functional groups and pore structure of the activated carbon (Bhatnagar et al., 2013). Despite overwhelming anticipation in water treatment, the biggest barrier of commercial activated carbon is the prohibitive cost and difficulty associated with regeneration. Other than that, large scale application for activated carbon will only raise the operational cost of a treatment plant due to the expensive cost of activated carbon over the years (Ali, 2010). Therefore, the drawbacks of commercial activated carbon have resulted in a growing research interest searching for low-cost alternative precursors for activated carbon as cheaper and renewable.

2.5.2 Limestone

Adsorption is one of the physico-chemical processes which used either activated carbon or low cost adsorbents such as limestone. Limestone adsorption has been widely used in drinking water treatment system because it is capable to remove low concentration of pollutants in the water after passing through several physicochemical treatments (Halim et al., 2010). In Malaysia, limestone is one the material that widely available and abundant in nature. Hence, limestone is likely to be an option as low cost adsorbent for removal of some pollutants in water or be combined with other treatment technologies (Martins et al., 2010).

Moreover, adsorption of limestone in drinking water treatment is done by using various sizes of limestone chips in a filter bed. Conventionally, limestone adsorption influent flows enter the bottom of a limestone retention tank. In addition, the flow