PERFORMANCE OF COMPOSITE ADSORBENT IN RIVER WATER TREATMENT

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ABSTRAK

Kajian ini dijalankan untuk menilai potensi media komposit yang terdiri daripada karbon aktif, batu kapur dan alginat sebagai pengikat dengan dua nisbah yang berbeza, bertujuan menyingkirkan pencemaran organik dan bukan org-anik yang diukur melalui kepekatan kekeruhan, warna dan Permintaan Oksigen Secara Kimia (COD) di dalam air sungai. Dalam kajian ini, sebelum penjerap komposit diuji, ciri-ciri pencemaran air sungai di Lubok Buntar telah diambil. Walau bagaimanapun, ciri-ciri air air sungai menunjukkan purata kepekatan COD yang rendah. Oleh itu, COD tidak diuji dalam eksperimen kumpulan. Daripada keputusan kajian kumpulan dan graf, faktor yang sesuai adalah 7g dos penjerap komposit, 180 RPM kelajuan goncangan, 75 minit masa sentuhan dan 90 minit masa pengenapan untuk nisbah 7: 3: 2 (AC: LS: AG). Sementara itu, bagi nisbah 1: 9: 2 (AC: LS: AG), faktor yang sesuai adalah 5g dos penjerap komposit, 180 RPM kelajuan goncangan, 95 minit masa sentuhan dan 40 minit masa pengenapan. Dari eksperimen kedua batching, bagi Nisbah 7: 3: 2, penyingkiran peratusan parameter adalah 92% untuk warna dan 85% untuk kekeruhan. Sementara itu, bagi Nisbah 1: 9: 2, penyingkiran peratusan parameter adalah 84% untuk warna dan 60% untuk kekeruhan. Ini menunjukkan bahawa 7: 3: 2 telah dipilih sebagai nisbah terbaik bagi penjerap komposit yang terdiri daripada karbon aktif, batu kapur dan alginat. Sementara itu, untuk setiap parameter, hasil daripada analisis model isoterm menunjukkan kesesuaian proses penjerapan dengan Isoterm Freundlich yang paling munasabah dengan hasil pekali yang tinggi untuk nilai penentuan pada ratio 7:3:2, manakala Isoterm Langmuir adalah sepadan untuk proses penjerapan pada ratio 1:9:2. Untuk kinetik penjerapan, bagi setiap parameter dan kedua-dua nisbah, kadar tindak balas jerapan dikawal oleh mekanisme kedua.

ABSTRACT

This study was carried out in order to access the potential of composite media by a combination of activated carbon, limestone, alginate as a binder with two different ratio, to remove organic and inorganic pollution that measured by concentration of turbidity, colour and Chemical Oxygen Demand (COD) in river water. In this present study, the batching experiment were conducted to decide the suitable factor for both ratio to effectively remove the involved parameter. Before the batching experiments, water characteristics were taken and COD were dismiss from batching experiment due to its low concentration. From the batch study, result and graph indicates that the suitable factor were 7g of dosage, 180 RPM of shaking speed, 75 minutes of contact and 90 minutes of settling time for ratio 7:3:2 (AC: LS: AG). Meanwhile for ratio 1:9:2 (AC: LS: AG), the suitable factor were 5g of dosage, 180 RPM of shaking speed, 95 minutes of contact time and 40 minutes of settling time. From the second batching experiments, for Ratio 7:3:2, the percentage removal of parameters were 92% for colour and 85% for turbidity. Meanwhile for Ratio 1:9:2, the percentage removal of parameters were 84% for colour and 60% for turbidity. This shows that 7:3:2 has been selected as the best ratio for composite adsorbent that consists of activated carbon, limestone and alginate. Meanwhile, the result from isotherms models for each of the parameters removal suggested that Freundlich isotherm was favourable with high coefficient of determination values for ratio 7:3:2 whereas the Langmuir isotherm were fit for adsorption process by ratio 7:3:2. For kinetic of adsorption, for each of the parameters removal by both ratios, pseudo-second-order model was suitable to describe kinetic of adsorption.

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LIST OF ABBREVIATIONS

AC	**A**ctivated **C**arbon
LS	**L**imestone
AG	**A**lginate
COD	**C**hemical **O**xygen **D**emand
NTU	**N**ephelometric **T**urbidity **U**nit
TCU	**T**rue **C**olour **U**nit
PtCo	**P**latinum **C**obalt

NOMENCLATURES

q_e	Amount of adsorbate adsorbed per unit mass of adsorbent
Ce	Equilibrium concentration of the adsorbate
C_f	Final concentrations of parameters
K_F	Freundlich adsorption constant
n	Freundlich heterogeneity factor
C_i	Initial concentrations of parameters
K_L	Langmuir adsorption constant
Qo	Maximum monolayer adsorption capacity of the adsorbent

CHAPTER 1

INTRODUCTION

1.1 Introduction

Clean and quality water is one of most vital resources, and when water is polluted it is not only give high impact to the environment, but also to human health. Much of that water comes from rivers, lakes and other surface water sources (Azlan et al., 2012). Contaminants in the water has been recognized to be a serious obstacles in order to delivering municipal uses and drinking water that public demand (Crittenden et al., 2012).

In recent years, a major interest were focused on the efficient techniques for the removal of highly toxic organic compounds from water (Rashed, 2013). A various methods such as coagulation, flocculation, filtration, and disinfection has been employed in the water treatment plants (Poitelon et al., 2010).

Among the possible techniques for water treatments, the adsorption technique by using solid adsorbents shows potential as one of the most efficient methods for the treatment and removal of organic contaminants in water and wastewater treatment. Adsorption has advantages over the other methods because of simple design and can involve low investment in term of both initial cost and land required (Rashed, 2013).

A selection for treatment process on aqueous solution were based on its contaminants and the ability of the treatment process to remove the contaminants. For river water, adsorption process shows a good performance on removal of major contaminants of river water which were organic, inorganic and microorganisms' contaminants (Abidin et al, 2016).

1.2 Background and Problem Statement

Among various research of treatment method of water and wastewater, adsorption process become a major interest due to its simplicity, economically viable, technically feasible and socially acceptable (Foo and Hameed, 2010).

In recent years, a greater interest is focused on the preparation of a new composite adsorbent material combining properties and advantage of activated carbon and low cost adsorbents, such as limestone to remove various pollutants. (Halim et al., 2012).

Another problem on the usage of activated carbon, which is usually in powder and granular form, is the difficulty on separating it from the effluent after treatment process, which may result in the loss of the sorbent. To overcome this problem, the encapsulation of Activated Carbon into alginate beads is a good solution which also combines the properties and advantages of each of their components (Rocher et al., 2010).

Hence, in this research project, a new composite adsorbent will be form by using activated carbon and limestone, encapsulate into alginate beads to treat the river water from Lubok Buntar. The selected parameter are colour, turbidity and chemical oxygen demand (COD). In order to get the optimum adsorption on these parameters, the ratio of the composite adsorbent and its removal conditions such as dosage of adsorbent, contact time, settling time and shaking speed shall be determined by via batch experiments.

Therefore, the purpose of this study is to obtain the suitable ratio for composite adsorbent which consists of activated carbon, limestone & alginate (as a binder) and to determine the best condition of the selected factors at the highest removal of the parameters such as colour, turbidity and chemical oxygen demand (COD).

1.3 Research Objectives

The research objectives of this study are listed below:

1. To determine the best condition of the selected factors at the highest removal of the parameters such as colour and turbidity.
2. To obtain the suitable ratio for composite adsorbent consisting of activated carbon, limestone & alginate (as a binder).

1.4 Scope and Limitation

In this research project, raw water samples were collected from river at Lubok Buntar, Bandar Baharu, Kedah. Water characteristics such as concentration of colour, turbidity, ammonia and COD including pH reading were determined. The water characteristics were analysed repetitively to obtain the average concentration of contaminants involved.

The first phase of this project were started on development of composite adsorbent by mixing activated carbon, limestone and alginate as a binder with 0.3 molarity of Calcium Chloride ($CaCl_2$).

Then, the second phase were on a batch experiment that was conducted to determine the best condition of important factors which are dosage of adsorbent, shaking speed, settling time and contact time. Another batch study was conducted to obtain the suitable ratio for composite adsorbent which consists of activated carbon, limestone & alginate. All data from batch study was analysed to determine the optimum factor and ratio. Besides that, the results from batch study also will be used to determine adsorption isotherm and kinetic of composite adsorbent.

1.5 Thesis Layout

This thesis contains five main chapters which explains different parts of this study on each chapter. Chapter one (1) elaborates on background and problem statement, research objectives and scope and limitation. Chapter two (2) is the literature review, which elaborates on collection of published information and data that relevant to this research. This chapter has also reviewed on the various treatment methods on surface water pollution, surface water treatment that includes adsorption process, adsorbent that has been used in treating river water and the adsorption techniques. Chapter three (3) is methodology, material used, scientific technique used to collect and evaluate data, preparation of composite adsorbent and experimental procedure. Chapter four (4) shows the results and discussions obtained from the experiments including the tables, graph and figure. Chapter five (5) is the final conclusion of the study, findings and recommendation for improvement of this study in future.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter consists of six sections. The first section explains about the river water pollution including the causes of pollution, the importance of water quality and sources that usually contaminate surface and river water such as colour, turbidity, ammonia, chemical oxygen demand (COD) and other contaminants. The second section discusses about treatments of river water including the types of treatment method, their applications and related parameters. The second section also discusses about the main focusses in this research project which is adsorption process and the factors affecting it. The third section discusses about composite adsorbent, material used and its potential in river water treatment. The fourth section elaborates about the adsorption isotherm, which consists the explanation of Langmuir and Freundlich isotherm. The fifth section discusses about the kinetic of adsorption including the description about pseudo first and second order. Lastly, the sixth section summarizes the literature review.

2.2 River Water Pollution

River water is potable sources which is fit for human consumption with minimum treatment. However, nowadays rivers are used as discharge routes for liquid and solid waste. Water pollution occurs when a water body are affected by discharged of small or large amounts of materials that contain pollutants to the water (Afroz et al., 2014).

River pollution is mainly caused by rapid urbanization, resulting from the development of residential, commercial, industrial and infrastructural facilities. However, the destruction of forests that affects natural water catchments, frequent soils erosion and heavily silted runoff, may as well resulting to river pollution. In other words, the main factors influenced the water quality in Malaysia are sediment run-off, industrial waste, domestic waste, agricultural, livestock and heavy metal (Amneera et al., 2013).

Pollutants in surface or river water can be determined by measuring the quality of water. Water quality is important as it determines the suitability of use and it can be analysed by its odour, colour, and concentration of organic and inorganic matters (Rahmanian et al., 2015). Besides, water quality is traditionally determined based on classification by considering physical, chemical, biological factors and heavy metals (Ay and Kisi, 2014). The classification of water usually can be determined by analysing the common principal or parameter that occurs on most water bodies such as pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), colour, ammonia, oxidised nitrogen (nitrite / nitrate), o-phosphate, chloride, major anions and cations, hardness, alkalinity and turbidity (Smith, 2013).

In this research project, turbidity, colour and COD has been selected as the parameter as it appears to be the main concern in treatment of river water due to several reasons that affects river and drinking water quality. Basically, excessive turbidity or cloudiness in drinking water is aesthetically unappealing and may represent a health concern as it supports the growth of pathogens. Turbidity in drinking water also can support pathogens breeding in the dissemination system, thus causing water-borne ailments such as gastroenteritis and other water-borne diseases (Aboubaraka et al., 2017).

Meanwhile, colour concentration in raw water also become a concern on water treatment in order to produce high quality water for municipal and drinking uses due to aesthetic aspects of the water. The uses of coloured water in municipal and drinking purpose even approved hygienically, is not acceptable worldwide due to every consumers that demand colourless water (Malakootian and Fatehizadeh, 2010). Usually, colour in water is concentrated with aromatic compounds produced from decay of organic matter. Undesirable taste and odour and disinfection by products are the reasons of colour existence in water. (Malakootian and Fatehizadeh, 2010).

Another parameter that is measured in this research is chemical oxygen demand (COD). COD is a commonly used indicator of water contamination and defined as the amount of oxygen required to oxidize all pollutants in a given volume of water (Yin et al., 2011). In other words, COD test predicts oxygen requirement during the decomposition of organic matter and the oxidation of inorganic chemicals (Amneera et al., 2013).

Hence, the measurement of turbidity, colour and COD indicates an important information in order to evaluate the removal potential and performance of composite adsorbent in river water treatment.

2.2.1 Turbidity

Turbidity is a principal physical characteristic of water. Due to natural and artificial activities, turbidity will occur to the water. It is caused by suspended matter or impurities that interfere with the clarity of the water. These impurities may include clay, silt, finely divided inorganic and organic matter, soluble colored organic compounds, plankton and other microscopic organisms (Jadhav and Mahajan, 2013). Technically, microorganisms that usually consists of bacteria, viruses and protozoa are typically attached to particulates, and removal of turbidity will significantly reduce microbial contamination in treated water (World Health Organization, 2011).

2.2.2 Colour

Colour in water consists of two types which are true colour and apparent colour. True colour is the result of soluble chemical substances that cannot be separated by filtration. Apparent colour that usually occurs in raw and surface water such as river water is the result of suspended and colloid solid that can be isolated by filtration. The presence of colour in water affects consumer assurance toward the quality of drinking water and consumer aesthetically do not accept coloured water (Malakootian and Fatehizadeh, 2010).

2.2.3 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) in water and wastewater is an important parameter for water quality control and environmental monitoring (Bogdanowicz et al., 2013). COD is an important index that measures the organic pollutant in water and it can be defined as the number of oxygen equivalents required to oxidize organic materials in water. (Latif and Dickert, 2015). Hence, the determination of COD is significant in water quality evaluation.

2.3 Treatments of River Water

Clean drinking water is essential to human and other living things. However, the sources of the clean drinking water are contaminated by chemical constituents such as organics, inorganics and gases and physical contaminants such as colour, odour and solid (Hasan et al., 2011).

In Malaysia, 99% of water used for domestic use were supplied from surface water such as river water, while another 1% of the supply from groundwater. However, municipal uses water, including drinking water consisting of untreated surface water and groundwater needs to be treated, before the water is made potable (Ab Razak et al., 2015).

Due to variety of events, such as storm water runoff or pollution that affected the surface water quality, the treatment processes used for groundwater and surface water treatment plants were generally different. Drinking water treatment plants employ various procedures in treatment method such as coagulation, flocculation, filtration, and disinfection, depending on source water quality due to different type of contaminants (Poitelon et al., 2010).

A research were developed simultaneously on a wide range of treatment methods such as precipitation, coagulation–flocculation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange with various levels of successes (Foo and Hameed, 2010). The process selection of a suitable treatment system is based on the contaminants involved and the ability of treatment process to remove the contaminants (Abidin et al., 2016).

2.3.1 Coagulation/Flocculation

Coagulation/flocculation is a commonly used process in water and wastewater treatment in which compounds such as ferric chloride or polymer are added to wastewater in order to destabilize the colloidal materials and lead the small particles to form larger settleable flocs. However, high operating costs due to the use of chemical substances and high amount of sludge and its disposal costs are shown as the important disadvantages of this chemical treatment (Ayguna and Yilmazb, 2010).

Coagulation/flocculation application usually includes removal of dissolved chemical species and turbidity from water via addition of conventional chemical-based coagulants such as alum, ferric chloride and polyaluminium chloride (Yin, 2010).

2.3.2 Filtration

Filtration process such as rapid gravity, bank filtration or slow sand filters are usually used to remove particulate matter from raw waters. Rapid gravity filters are usually used to reduce turbidity which include adsorbed chemicals, oxidized iron, manganese from raw waters and commonly used to remove floc from coagulated waters. Slow sand filters are more suitable for low-turbidity water or water that has been pre-filtered. They are used to remove algae and microorganisms, including protozoa, and to reduce turbidity, if preceded by micro straining or coarse filtration (World Health Organization, 2011).

2.3.3 Chlorination

Chlorination is one of many methods that can be used to disinfect water. Along with other water treatment processes such as coagulation, sedimentation, and filtration, chlorination creates water that is safe for public consumption. Chlorination usually treats microorganisms such as pathogens, a harmful group of organism that can be found in raw water from rivers, lakes and groundwater. Chlorination may also be done as the final step in the treatment process, which is when it is usually done in most treatment plants. Chlorination method usually control the biological growth, remove iron and manganese, remove taste and odours, control algae growth, and remove the colour from the water (Safe Drinking Water Foundation, 2017).

2.3.4 Adsorption

Among various treatment method, a major interest were focused on adsorption process, as the most efficient, promising and widely used fundamental approach in wastewater and water treatment processes (Foo and Hameed, 2010).

Additionally, amongst the various techniques in water treatment, adsorption is the method of choice because of its ease of operation and design (Umoren et al., 2013). Compared to alternative technologies, adsorption is attractive for its relative simplicity of design, operation and scale up, high capacity and favourable rate, insensitivity to toxic substances, ease of regeneration and low cost. Moreover, adsorption process avoids using toxic solvents and minimizes degradation (Soto et al., 2011).

Adsorption process that usually involved Activated Carbon as adsorbent has being recognised as one of the most effective technologies at removing natural organic matter from water in treatment plants that supply water for municipal uses (Gibert et al, 2013). Moreover, Activated carbon adsorption has shown a good performance in removing organic matter and turbidity (Hatt et al., 2012).

2.3.5 Factor Affecting Adsorption Process

Adsorption is a surface phenomenon by which a multi-component fluid, whether gas or liquid mixture was attracted to the surface of a solid adsorbent and forms attachments via physical or chemical bonds (Foo and Hameed, 2010). In other words, Rashed, (2013) explains that adsorption process occurs when contacting solid with a highly porous surface structure with a solution containing absorbable solute, a liquid–solid intermolecular forces of attraction occurs resulting some of the solute molecules from the solution to be concentrated or deposited at the solid surface.

Water treatment by adsorption process were optimized considering various factors such as characteristics of adsorbent and adsorbates, contact time, concentration of adsorbate, pH, dose of adsorbent, particle size of adsorbent, temperature and the presence of other pollutants (Ali, 2014).

Considering that several conditions and factors that affecting adsorbent performance of adsorption, dosage of adsorbent, contact time and shaking speed between adsorbent and adsorbate including settling time are important and need to evaluate. These factors are important in order to indicate the removal percentage of parameters in optimum uses of composite adsorbent (Kamaruddin, 2015).

2.4 Composite Adsorbent

The high contaminants in natural waters that was occurs since 1960s has led to origination of adsorption by activated carbon, as one of the most effective method in removing these substance in wastewater or natural water (Faust and Ally, 2013). However, its expensive regeneration and disposal problems are the major disadvantages of activated carbon (Hussain et al., 2011). To overcome the problem, Halim et al. (2012) suggested on the preparation of a new composite adsorbent material combining excellent properties such as activated carbon and low cost adsorbents like limestone to remove various pollutants.

A research conducted by Aziz et al. (2011) that suggests a mixture of limestone and activated carbon in highly coloured and turbid wastewater was resulting up to 88% removal percentage of colour and turbidity. To combine the properties and advantage of each component such as limestone and activated carbon, Rocher et al. (2010) suggests encapsulation of various type of adsorbent into alginate beads.

2.4.1 Activated Carbon

Activated carbon are highly effective adsorbents for removing organic pollutants in the aqueous or gaseous phase, and widely applied in the purification of water and air (Halim et al., 2012). Activated carbon is widely used to control odor or taste and remove contaminants in water treatment processes because of its huge specific surface area and well-developed pore structures (Chang et al., 2010).

Activated carbon has long being recognised as one of the most effective materials at removing natural organic matter from water in drinking water treatment plants (Gibert et al, 2013). A research conducted by Hatt et al. (2012) shows that activated carbon has succesfully removed at least 80% of organic matter and turbidity in water treatment.

2.4.2 Limestone

Limestone has been widely used in drinking water treatment by using sorptive filtration system and has shown a good performance (Murutu et al., 2010). Limestone has shown its effectiveness in treatment process involving aqueous solution with high colour concentration (Aziz et al, 2011). A suggestion to combine low cost adsorbents like limestone with activated carbon were recommended to reduce cost and to remove various pollutants as it also combining excellent properties of each materials (Halim et al., 2012).

2.4.3 Alginate

Alginate will be used in this research project as a binder for composite adsorbent consists of activated carbon and limestone. Alginate is often mixed with commercial adsorbent in order to improve the adsorption characteristics as well as to modify its physical and chemical features (Kamaruddin, 2015).

Nowadays, there are various type of adsorbent in different forms such as powder or granular form which has been developed in order to effectively remove the contaminants in the water. The application of powder adsorbents to the treatment of wastewater has often been confronted with limitations due to the dispersion and inability to recollect the powder from treated water. In order to overcome this problem, alginate gel has been used with adsorbents to impregnate or encapsulate reactive materials or adsorbent, such as activated carbon to form alginate complexes beads (Choi et al., 2012).

Moreover, previous studies shows a good performance in encapsulation of adsorbent into alginate beads that can combine the properties and advantages of each of components in composite adsorbent (Rocher et al., 2010). Besides its function as the binder of adsorbent reactive materials, Alginate is very effective in turbidity removal generally over 98%, depends on the turbidity contains in the water and the viscosity of Alginate (Devrimci et al., 2012).

2.5 Adsorption Isotherm

Adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by adsorbent. The relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium can be determine by using adsorption isotherm model. Moreover, adsorption ishotherm also shows the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations (Desta, 2013).

Adsorption isotherm is very important in describing the relationship between the adsorbate and adsorption. Moreover, the adsorption capacity of the adsorbent, which is an important parameter in the industrial design for adsorption process can be predicted by using isotherm analysis. Two well-known Isotherm model, Langmuir and Freundlich Isotherm were used in this research project. The Langmuir model explains the monolayer adsorption process that occurs on the homogeneous adsorbent surface. Meanwhile, the Freundlich isotherm presumes that the multilayer of the adsorption process occurs on a heterogeneous surface (Benhouria et al., 2015).

2.5.1 Langmuir isotherm model

The Langmuir isotherm was developed on the assumption that the adsorption process takes place at specific homogeneous sites. Once a molecule occupies a site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer (Chen et al, 2010). In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. Langmuir isotherm refers to homogeneous adsorption, which each possess equal bonding for the adsorbate which means every molecules energetically equivalent to each other in respect (Foo and Hameed, 2010). The Langmuir isotherm equation (Halim et al, 2010), is expressed by the following equation;

$$q_e = \frac{Q_0 K_L C_E}{1 + K_L C_E} \qquad \text{(Equation 2.1)}$$

The linear form of Langmuir isotherm equation were shown in the equation below (Aziz et al., 2011).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_E \qquad \text{(Equation 2.2)}$$

From the equation above, 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_0 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).

2.5.2 Freundlich isotherm model

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces (Kamaruddin, 2015). In the Freundlich Isotherm perspective, the amount adsorbed is the summation of adsorption on all sites, which each sites having bond energy, with the stronger binding sites are occupied first, until adsorption energy are exponentially decreased upon the completion of adsorption process (Foo and Hameed, 2010).

The Freundlich isotherm equation (Halim et al, 2010), is expressed by the following equation;

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

The linear form of Langmuir isotherm equation (Aziz et al., 2011) was expressed by Equation 2.4;

$$\log q_e = \log K_F + \frac{1}{n} \log C_E \qquad \text{(Equation 2.4)}$$

From the equation, 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 $(\mathrm{mg/g})(\mathrm{L/mg})^{\frac{1}{n}}$ and n is the Freundlich heterogeneity factor.

2.6 Kinetics of Isotherm

Kinetic models are useful in determining the significance of diffusion mechanisms and the estimation accuracy of the diffusivities inside the adsorbent particles (Kamaruddin, 2015). The kinetics of adsorption is important because it controls the efficiency of the process and the equilibrium time. It also describes the rate of adsorbate uptake on adsorbent (Chen et al., 2010).

2.6.1 Pseudo-first-order kinetics model

The pseudo-first-order equations, or also known as Lagergren-first-order kinetic model (Zhu et al., 2010), can be expressed by following equation (Kamaruddin, 2015);

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{(Equation 2.5)}$$

For the boundary conditions t=0 to t and q_t=0 to q_t, gives the following equation:

$$\log(q_e - q_t) = \log q_e \frac{k_1 t}{2.303} \qquad \text{(Equation 2.6)}$$

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) (Kamaruddin, 2015).

2.6.2 Pseudo-second-order kinetics model

The pseudo-second-order equations that are based on equilibrium adsorption can be expressed as following equation (Kamaruddin, 2015);

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \text{(Equation 2.7)}$$

The linear form of Langmuir isotherm equation is given by Equation 2.4;

$$\frac{dq_t}{dt} = \frac{dq_t 1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad \text{(Equation 2.8)}$$

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) (Kamaruddin, 2015).

2.7 Summary of Literature Review

Based on literature review, adsorption is a major interest of treatment process as highly efficient, promising and widely used fundamental approach in water treatment processes. It has a wide potential in treatment of river water which are polluted by organic, inorganic and microorganism contaminants. Amongst various techniques in water treatment, but adsorption is the method of choice because of its ease of operation and design. This chapter presents an overall literature review of previous study involving removing potential of parameters in raw water and wastewater by several materials used in composite adsorbent. It also indicates that effectiveness of the contaminant involves in other treatment method.

From the literature review, we can indicate that by using alginate as a binder or in other word the encapsulation of several adsorbent, has been used effectively in water purification. Alginate beads solves the regeneration, dispersion and lack of selectivity problem of activated carbon. Limestone that has been well known as the low-cost adsorbent also will be combine with activated carbon and alginate to form a new composite adsorbent. In this research project, the performance of limestone to remove the turbidity, colour and COD can be measure as its potential to remove those parameter was rarely investigate. To achieve an optimum removal of parameter due to removal selectivity of different materials, the composite adsorbent will be classified into two different ratio. The ratio are 7:3:2 and 1:9:2 for activated carbon, limestone and alginate respectively.

Meanwhile, the literature review also shows that batch studies indicate useful information on the optimization of factor that affecting adsorption process such as dosage of adsorbent, shaking speed, contact time and settling time in parameter removal. This chapter also discussed adsorption isotherm and kinetics including its importance in explanation of adsorption process.

CHAPTER 3

METHODOLOGY

3.1 Overview

This chapter describes about the study area where the sampling process took place. The characteristics of the river water is discussed and referred to the guideline 'Drinking Water Quality Standard' published by Ministry of Health Malaysia (MOH). The methods and procedures used in determining the characteristics of river water will be explain in this chapter.

This chapter also elaborates on the physical and chemical procedures in preparation of composite adsorbent consisting of activated carbon, limestone and alginate. The procedure of batch experiments, apparatus and machines used also will be explain in this chapter.

Finally, this chapter also mentions about the procedure of determining removal percentage of parameter involves, which are colour, turbidity and chemical oxygen demand (COD).

3.2 Experimental Flow

This research project consists of two major phases, preparation of composite adsorbent and batching experiments. The experimental flow in figure 3.1 shows the steps and sequence of work that was performed during the study.

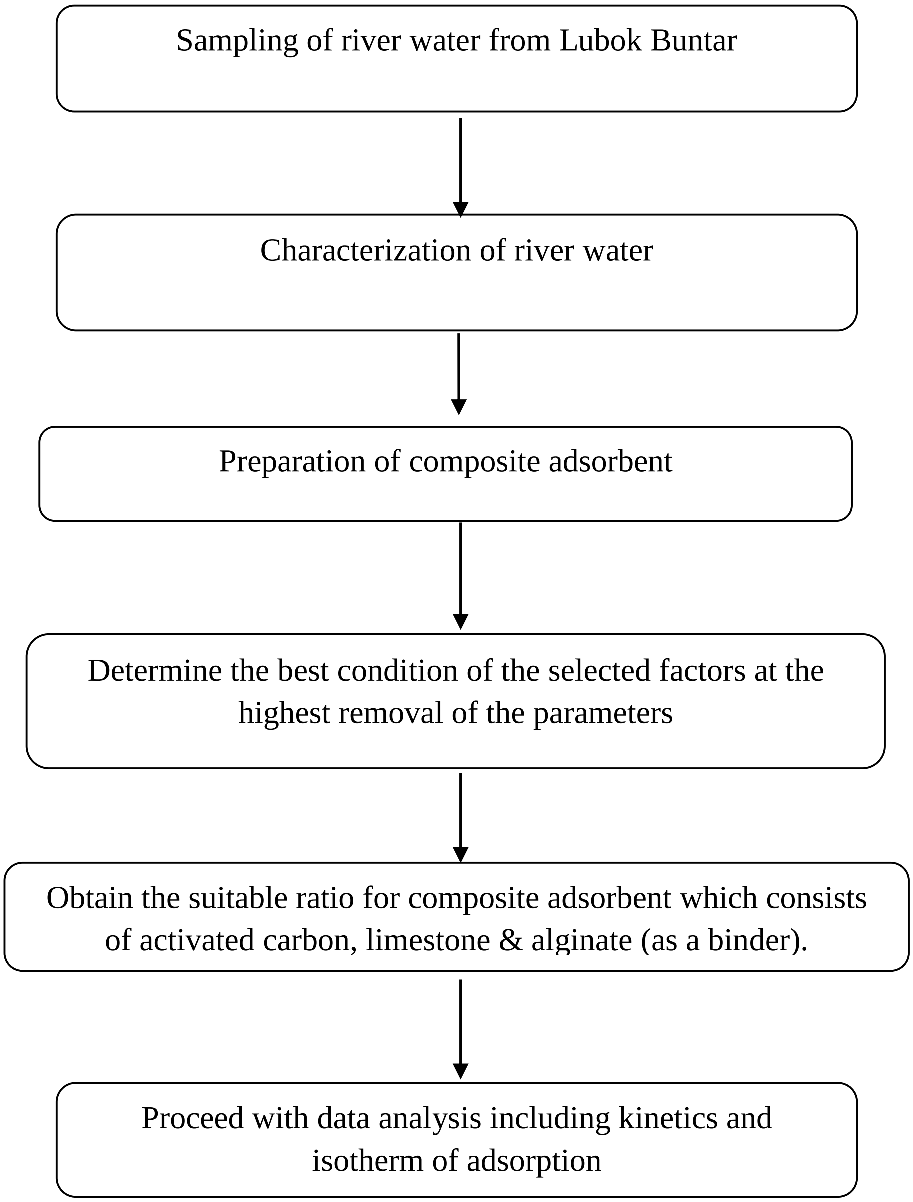

Figure 3.1: Experimental flow

3.3 Materials and Chemicals

Materials and chemicals used for the experiments in this research project are shown in the Table 3.1 below. All experiments were conducted at Environmental Laboratory 1, School of Civil Engineering, Universiti Sains Malaysia.

Table 3.1: Materials and chemicals used for preparation of composite adsorbent and batch experiment.

Experiment	Materials	Chemicals
Preparation of sample and batch study	Mechanical stirrer, hot plate, 500mL beaker, bead injector, air tight container, orbital shaker, stop watch.	Calcium chloride ($CaCl_2$)
PH test Colour Test Turbidity Test	pH meter, YSI Probe, DR 2800 spectrophotometer, HACH 2100N turbidimeter, filter paper, conical flask, filter funnel, sample cell 10ml, beaker, distilled water, tissue	None
COD Test	COD digester, DR 2800 spectrophotometer, COD vials, pipette, sample cell 10ml, tissue	potassium dichromate, sulphuric acid, silver sulphate, mercury sulphate
Ammonia Test	DR 2800 Spectrophotometer Sample cell 25ml, pipette	mineral stabilizer, polyvinyl alcohol, Nessler reagent

3.4 Sampling of River Water

River water samples were collected from Kerian river, Lubuk Buntar, which is located at Bandar Baharu within 5˚08'14.1"N and 100˚35'09.8"E. The water samples for laboratory test were collected from river water surface by using grab sampling and collected into sample bottles. The water sample were taken 5 times. To obtain the characteristics of river water, the concentration of colour, turbidity, ammonia and COD including pH values and water temperature were taken before the evaluation of composite adsorbent.

3.5 Characterization of River Water

River water sample was tested and analysed in the Environmental Laboratory, School of Civil Engineering, Universiti Sains Malaysia. Then, a comparison of characteristics of river water and National Standard for Raw and Drinking Water Quality (Ministry Of Health Malaysia, 2000) were made, as shown in Table 3.2. The turbidity of the sample was measured using HACH 2100N Turbidimeter. For characterization of colour, ammonia and COD, the instrument used was HACH DR 2800 Spectrophotometer.

Table 3.2 Standards of selected parameters for Drinking Water Quality (Ministry Of Health Malaysia, 2000)

Parameter	Unit	Malaysia National Guidelines for Raw Water Quality	Malaysia National Guidelines for Drinking Water Quality
Turbidity	NTU	1000	5
Colour	PtCo	300	15
COD	mg/L	10	-
Ammonia	Mg/L	1.5	1.5
pH	-	5.5 – 9.0	6.5 – 9.0

3.5.1 Turbidity Measurement

For measurement of turbidity in the laboratory, HACH 2100N Turbidimeter was used to determine the turbidity of water samples. Distilled water was used as blank sample in this experiments. Both blank sample and water samples were poured into 10ml glass cells. Firstly, the glass cell contains blank sample was put into the place holder and zero button was pressed. Then, remove the blank sample and the glass sample cell contains water sample was put into the place holder and the reading was read out from the display in a few second. The reading was obtain by using Nephelometric Turbidity Unit (NTU) (APHA et al, 2012).

3.5.2 Colour Measurement

For measurement of colour in the laboratory, apparatus used was HACH DR 2800 Spectrophotometer with Standard Method 120 (APHA et al, 2012) with the HACH programmed number of 125 and the wavelength was calibrated at 465 nm. The amount of water samples required for a glass sample cells is 10ml. Then, 10ml distilled water was required to be prepared in order to become blank sample. The blank sample was put into the instrument prior to both water samples in order to get reference as zero reading. The reading was obtain by using Platinum-Cobalt scale (PtCo) (APHA et al, 2012).

3.5.3 COD Measurement

For measurement of chemical oxygen demand (COD) in the laboratory, apparatus used was HACH DR 2800 Spectrophotometer with the HACH programmed number of 125 and the wavelength was calibrated at 465 nm. The amount of water samples required for a glass sample cells is 10ml. Then, 10ml distilled water was required to be prepared in order to become blank sample. Both river and distilled water were put in the prepared COD vial that also contain potassium dichromate, sulphuric acid, silver sulphate and mercury sulphate. Both vials contain river and distilled water was condensed in the COD reactor as shown in figure 3.5 for 2 hours. After 2 hours, invert each vials several times and cool both in room temperature. Then, the blank sample was put into the HACH DR