AGROWASTE BASED CARBON ADSORBENT FOR DYES REMOVAL: EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

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By

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TABLE OF CONTENT

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: MATERIALS AND METHODS

CHAPTER FOUR: RESULTS AND DISCUSSIONS

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF SYMBOLS

Symbol		**Unit**
A	Arrhenius factor	-
A_T	Equilibrium binding constant	L/mg
β	Extent of surface coverage and activation energy for chemisorptions	g/mg
β_o	Constant of RSM linear equation	-
β_i	Coefficient of RSM linear equation	-
β_{ii}	Quadratic parameters coefficient	-
β_{ij}	Interaction parameters coefficient	-
B	Constant for Temkin equation	-
B_{DR}	Constant for Dubinin-Radushkevich isotherm	-
B_t	Constant for Boyd model	-
C	Boundary layer	-
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Highest initial adsorbate concentration	mg/L
C_t	Dye concentration at time, t	mg/L
E	Mean free energy	J/mol
E_a	Arrhenius activation energy of adsorption	kJ/mol
k_1	Adsorption rate constant for the pseudo-first-order kinetic	1/min
k_2	Adsorption rate constant for the pseudo-second-order	g/mg.min
K_{dif}	Intraparticle diffusion rate constant	mg/g.min$^{1/2}$
K_F	Freundlich isotherm constant	mg/g (L/mg)$^{1/n}$
K_L	Langmuir sorption constant	L/mg
K_T	Standard thermodynamic equilibrium constant	L/g
M	Mass of adsorbent	g
n_F	Constant for Freundlich isotherm	-

q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Adsorption capacity of Langmuir isotherm	mg/g
q_s	Constant for Dubinin-Radushkevich isotherm	mg/g
q_t	Amount of adsorbate adsorbed at time, t	mg/g
Q_m	Maximum adsorption capacity	mg/g
R	Universal gas constant	8.314 J/mol K
R_L	Separation factor	-
R^2	Correlation coefficient	-
T	Absolute temperature	K
t	Time	min
V	Solution volume	L
$\Delta H°$	Changes in standard enthalpy	kJ/mol
$\Delta S°$	Changes in standard entropy	kJ/mol
λ	Wavelength	nm

LIST OF ABBREVIATION

AC	Activated Carbon
BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infrared
IUPAC	International Union of Pure and Applied Chemistry
MB	MB Methylene blue
N	No visible floatable materials or debris or no objectionable odour, or no objectionable taste
PS	Peanut shell
PSAC	Peanut shell based activated carbon
RBBR	Remazol brilliant blue R
rpm	Rotation per minute
SEM	Scanning electron microscopy

PENJERAP KARBON BERASASKAN SISA PERTANIAN UNTUK PENYINGKIRAN PENCELUP: KAJIAN KESEIMBANGAN, KINETIK DAN TERMODINAMIK

ABSTRAK

Tujuan kajian ini adalah untuk mengkaji kebolehlaksanaan karbon teraktif berasaskan kulit kacang tanah (KTKKT) dan karbon teraktif berasaskan tangkai buah kelapa (KTTBK) dalam penyingkiran pewarna metilena biru (MB) dan remazol biru berkilau R (RBBR) dari larutan akuas. Pengaktifan fizik-kimia merangkumi impregnasi oleh kalium hidroksida (KOH) diikuti oleh gasifikasi karbon dioksida (CO_2) telah digunakan untuk menghasilkan KTKKT dan KTTBK. Keadaan optimum penyediaan KTKKT adalah pada suhu pengaktifan 653^oC, masa pengaktifan 0.75 jam dan nisbah jerap isi 1, manakala 673^oC, 0.79 jam dan nisbah jerap isi 0.85 untuk KTTBK. Kesan kepekatan awal pewarna (50-500 mg/L), masa penjerapan (0 - 24 jam), suhu larutan (30 – 60^oC) dan pH larutan (3 – 11) terhadap penjerapan pencelup ke atas permukaan KTKKT dan KTTBK telah dinilai. *Freundlich* didapati berpadanan dengan keputusan keseimbangan dalam penyingkiran MB dan RBBR oleh kedua-dua karbon teraktif. Penyingkiran pencelup-pencelup dengan menggunakan KTKKT dan KTTBK masing-masing adalah berpadanan dengan model kinetic pseudo tertib kedua dan pseudo tertib pertama. Tenaga pengaktifan untuk kesemua proses penjerapan adalah rendah daripada 40kJ/mol menunjukkan penjerapan berlaku secara jerapan fizikal.

AGROWASTE BASED CARBON ADSORBENT FOR DYES REMOVAL: EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

ABSTRACT

The aim of this work is to investigate the feasibility of peanut shell based activated carbon (PSAC) and coconut peduncle based activated carbon (CPAC) for methylene blue (MB) and remazol brilliant blue R (RBBR) removal from aqueous solution. Physiochemical activation consisting of potassium hydroxide (KOH) impregnation and carbon dioxide (CO_2) gasification were used to prepare PSAC and CPAC. The optimum preparation conditions were 653°C, 0.75 hour and impregnation ratio (IR) of 1 for PSAC whereas 673°C, 0.75 hour and IR of 0.85 for CPAC. The effect of initial dye concentration (50 – 500 mg/L), contact time (0 - 24 hour), solution temperature (30 - 60 ℃) and pH of solution (3–11) onto dyes removal were evaluated. Freundlich model was found best suited for MB and RBBR adsorption for PSAC and CPAC. Dyes adsorption with PSAC and CPAC were best suited the pseudo-second-order kinetic model and pseudo-first-order kinetic model, respectively. The activation energy for all adsorption processes showed values lower than 40 kJ/mol indicating the physisorption mechanism in adsorption.

CHAPTER ONE

INTRODUCTION

1.1 Dyes effluent and treatment

Textile industry uses dyes as the main material for coloring their final products such as cotton, silk, linen and wool nylon. This industry has been known as one of the major source of water consumption and water pollution (Khelifi et al., 2009). The effluents from this industry contain large amounts of dyes which are highly toxic (Baskaralingam et al., 2007).

Different methods of treatment have been developed in order to reduce the impact of dyes to the environment. Biological method uses bacteria to biodegrade dye particles in wastewater. The effectiveness of removing dyes biologically varied depends on temperature, retention time and chemical substance in the wastewater. Besides, large space is required for dyes removal using biological method. Membrane filtration and electrochemical methods have been applied for dyes removal from wastewater. However, these techniques suffer from same drawbacks such as the disposal of the high capital cost and time consuming (Garba et al., 2014).

Liquid-phase adsorption is one of the methods for dyes removal that has been found to be efficient in terms of flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (de Luna et al., 2013). In addition, adsorption does not result in the formation of harmful substance. Special characteristic of activated carbon such as high adsorption capacity and surface area make it suitable to be used in dyes effluent treatment. Physical adsorption is considered more effective and superior compared to former techniques (Yu and Luo, 2014). By referring to the abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent (Crini, 2006). Activated carbon has been proven to be an effective and widely used adsorbent for the removal of a variety of organic and inorganic pollutants dissolved in aqueous media (Dias et al., 2007).

Peninsular Malaysia generates large amounts of wood and agricultural residues, the bulk of which are not being currently utilised for any further downstream operations. In Malaysia, peanut production reaches 2000 metric ton in year 2013 and still growing as reported by Index Mundi. While on the other hand, coconut production reaches 22, 000 metric ton in year 2013 as reported in Index Mundi. The agricultural waste is used either as fuel for the kiln drying of timber, for the manufacture of bricks, the curing of tobacco leaves, the drying rubber-sheets and for the manufacture of products such as particleboard and fibreboard. The rest has to be disposed of by burning. For an economical wastewater treatment purpose, therefore the development of activated carbon from no-cost agrowaste material acquired locally is an interesting option.

1.2 Problem statement

The presence of dyes in aquatic environments has been of great concern due to their toxic nature and intensively colored with complex molecular structures that can affect light penetrations and upsetting biological processes in that particular stream (Gómez et al., 2007). These dyes are toxic to living organisms and may cause damage to the human organs such as kidneys, reproductive system, liver, and central nervous system.

Basic dye is one of the most commonly used dye but it is known to cause harmful effect to human being and other aquatic organisms as well. On the other hand, reactive dyes are used extensively in textiles industry, primarily utilized for tinting fibres. However, reactive dyes pose the greatest problem in textiles wastewater since in both ordinary and hydrolysed forms are not easily biodegradable, and thus, even after extensive treatment, colour may still remain in the effluent which is also toxic to aquatic life. In fact, limited studies have been reported on the removal of reactive dyes especially using activated carbon prepared from tropical fruit wastes. Therefore, the adsorptions of both types of dyes were studied onto the activated carbon prepared.

Malaysia is blessed with abundance of organic resources which are often regarded and disposed as wastes (El-Hendawy, 2005). Recent research shows that these valuable materials can be converted into precious adsorbent which is useful for dyes treatment (Halim et al., 2012). The amount of tropical fruit wastes generated in Malaysia is increasing enormously due to the high demand in production of processed fruits products. It is well-known that most of the tropical fruit wastes which are available in Malaysia have little or no economic value and cause a serious problem to local environments. Conversion of these tropical fruit wastes into activated carbons which can be used as adsorbents in water purification or the treatment of industrial and municipal effluents in Malaysia would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial activated carbons. In this work, the dyes removal was studied using activated carbon adsorbent prepared from peanut shell and coconut peduncle.

1.3 Objectives of research

The objectives of the research are:

1. To optimize the physiochemical activation conditions to prepare peanut shell based activated carbon (PSAC) and coconut peduncle based activated carbon (CPAC).
2. To study the effects of initial dyes concentration, contact time, temperature and solution pH on the adsorption of methylene blue (MB) and remazol brilliant R (RBBR) dyes onto PSAC and CPAC.
3. To study the adsorption isotherm, kinetic and thermodynamic for dyes adsorption onto PSAC and CPAC.

1.4 Scope of study

In this work, peanut shell and coconut peduncle were used for activated carbon production by physiochemical activation process which included KOH impregnation and heating with CO_2 gasification. The preparation conditions (impregnation ratio, temperature and time) of activated carbons were optimized by using response surface methodology (RSM). From the optimization result, the samples were characterized in terms of surface area, proximate analysis, morphology and surface chemistry. The samples were then tested for removal of methylene blue (MB) and remazol brilliant blue R (RBBR) from aqueous solution in batch adsorption system. The initial concentration, time, solution pH and temperature were varied in order to analyse for dyes adsorption equilibrium, kinetics and thermodynamic studies onto the samples.

1.5 Organization of the thesis

This thesis is divided into five main chapters which covered the work done in addition to the appendices. Chapter 1 introduced the dyes effluent, problem statement, research objectives and scope of study.

Chapter 2 review the general definition of each types of dyes used in adsorption process, methods of dye removal, and raw material used in preparing activated carbon. Moreover, the factors that affect adsorption process, optimizing of operating parameters, adsorption isotherms, kinetics and thermodynamic parameters will also be discussed in this chapter.

Chapter 3 included the methodology and materials used in the experiment. This chapter will discuss on the general description of batch adsorption experiment, equipment and materials used. Other than these, the experimental procedure and the description of factors affecting the adsorption process will be presented.

Chapter 4 included the experimental results as well as the discussion of the results. This chapter will also further elaborate on the effect of different factors on batch system adsorption. The result on equilibrium, kinetic and thermodynamic studies will be given in this chapter.

Chapter 5 conclude all the observation and result obtained from the experiment and discussion on the previous chapter (Chapter 4). Suggestion and recommendation will be discussed in this chapter also.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes in textile industries

There are more than 100,000 types of commercially available dyes with estimated 7×10^5 tonne are produced annually (Pearce et al., 2003). Two types of dyes that are commonly used in textile industry are basic dye and reactive dye. The basic dye is a cationic soluble dye which is used to bind to negatively charged tissue components such as nylon, polyester, and fibre. Basic dye such as methylene blue (MB) and malachite green (MG) is usually characterised by heterocyclic aromatic chemical compound. Basic dyes consist of amino groups, or alkylamino groups, as their auxochromes. Basic dyes predominantly have delocalised positive charges on their chromophore which are concentrated at amino group (El Qada et al., 2008). Methylene blue is one of basic dyes that have been widely used for medication, textile industry, paper, and for analysis. Methylene blue causes difficulty in breathing when inhaled. Sickness like vomiting, diarrhoea, nausea and burning sensation are experienced when methylene blue is being orally ingested.

Remazol brilliant blue R (RBBR), remazol brilliant violet 5R (RBV5R) and remazol brilliant red (RBR) are types of reactive dye that are commonly used to dye cotton, wool, silk and nylon. It simplifies the dyeing process and improves fastness of the colouring. It attach to the substrate by forming a covalent bond between the molecules. The dye becomes a part of the fibre which is much less likely to be removed by washing. Reactive dyes is very difficult to be removed due to its high solubility in water (Baskaralingam et al., 2006).

Methylene blue is a popular dye that is extensively used. Its application extends to medical sciences but is highly toxic and pollutes the environment. Meanwhile, among the synthetic dyes, about 70% of the worldwide market used by dyeing industries is composed of reactive dyes. It Is the largest group of organic dyes that are considered to be difficult to degrade even at low concentration due to its high resistant to light, heat, water, chemical and microbial attack (de Luna et al., 2013). Hence, it is very important to remove both basic and reactive dyes from wastewater effluents before it is discharged into water bodies.

2.2 Dye removal techniques

Dyes are considered a “hard-to-treat” pollutant due to its persistence to degradation. It is striking visible in recipient and influence photosynthetic activity of aquatic lives. The accumulation of dyes in certain forms of aquatic life may lead to toxic products. Various ways of dyes removal techniques have been developed such as membrane filtration, coagulant-flocculent, biological method and adsorption in order to overcome the considerable amount of dyes in textile industry.

Membrane filtration is considered quite effective because of their high efficiency in dye removal. However, the drawback of this method is a limited lifetime before membrane fouling occurs and high cost of periodically membrane replacement is required.

In coagulation-flocculation process, the concentrated sludge is formed which accumulates after the treatment and end up with disposal problem. The effectiveness of coagulation-flocculation method depends on pH of wastewater to be treated. Before the method is applied, the pH of the wastewater needs to be adjusted for the lowest solubility of the substance that needs to be removed.

Biological method involves growth of bacteria and some microorganisms to remove dyes where the bacteria are able to grow and provide energy for microbial metabolism which consume the dyes in wastewater. Dyes as raw material for microbial metabolic activity are removed as by-product. Biological method is more secure, economic and environmental friendly compared to chemical and physical method. However, there are problems rises such as excessive growth of bacteria, which cause clogging to the pipeline. Bacteria used in wastewater treatment are also sensitive to agitation and chemical inside the wastewater. Pretreatment for the wastewater is needed before undergo biological method because biodegradation rate of dyes is very slow. Moreover, it has worse performance in a continuous reaction as more time for the bacteria is needed to remove the dye in batch reactor. In addition, bacterial contamination can destabilize its performance too. Usually stabilizer is needed for the wastewater to maintain the highest efficiency of dye removal. Biological method is ineffective in color removal, low flexibility in operation and design and may require large areas for the process (Fayidh et al., 2011). Table 2.1 shows some advantages and disadvantages of a few types of dye removal methods.

Table 2.1 Techniques for dye removal

Technology	**Advantages**	**Disadvantages**
Coagulant/ Flocculants	Simple, economically feasible	High sludge production, handling and disposal problems
Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirement
Adsorption	Great capacity, produce a high-quality treated effluent	Expensive adsorbent, difficulties in adsorbent loading and unloading
Membrane Separation	Remove all dye types, produce a high-quality treated effluent	High pressure, expensive, incapable of treating large volumes

Adsorption process is commonly used in treating industrial wastewater due to ease of operation, flexibility, simplicity of process and does not easily affect by toxic pollutants. In addition, adsorption does not produce harmful material after the reaction. The adsorption technique is found more effective compared to other techniques such as coagulation, flocculation, precipitation and activated sludge for wastewater treatment.

2.3 Adsorption

Adsorption occurs when gas or liquid solute accumulates on the surface of adsorbate such as activated carbon. Adsorption process occurs at the interfacial layer of the adsorbent and adsorbate. There are two types of sorption which are physisorption and chemisorption. Physisorption is physical adsorption where the adsorbate adheres to the surface of adsorbent through only weak Van der Waals interactions between the molecules. Chemisorption is an adsorption where the adsorbate adheres to the surface of adsorbent through the formation of strong chemical bond.

Adsorption is affected by the solubility of adsorbate in solution. Substance with slightly soluble in water can be more easily removed from solution. The performance of adsorption is affected by the initial adsorbate concentration where for high initial concentration produced high driving force of mass transfer initially. This process is strongly depends on contact time between adsorbate and adsorbent in order to achieve the equilibrium. The adsorption process is also strongly dependent on solution temperature. If the adsorption capacity increases at higher temperature, the adsorption is an endothermic nature where the adsorbate gains more energy for the binding to the active site of the adsorbent. However, if the adsorption capacity increases with decreasing in temperature, the adsorption process is an exothermic process. This is due to the weakening in bonding between adsorbate and adsorbent at high temperature. Solution pH is also affecting the effectiveness of adsorption process. This is due to the amount of positive and negative charges that exist in the solution. These charges affect the adsorption process through dissociation of functional groups of the active sites on the surface of the adsorbent which can be account on the basis of surface hydroxylation, acid-base dissociation and surface complex formation.

2.3.1 Activated carbon

Activated carbon has high internal surface area (>600 m^2/g) and porosity which makes it ideal for adsorption process. The porosity could be divided into three groups which are macropores, mesopores and micropores. According to International Union of Pure and Applied Chemistry (IUPAC), the macropores represent pores of a width larger than 50 nm, mesopores are pores between width 2 to 50 nm and micropores are defined as pore less than 2 nm.

There were two steps in preparing activated carbon namely carbonization and activation. The first step was to turn the raw material into char where the volatile matter and moisture content were removed. After carbonization process, the raw material was turned into solid char (Li et al., 2008). The second step was to activate the char produced. Activation process was carried out at high temperature to further remove volatile matter and create the porosity on the sample’s surface. This leads to the increase in the surface area of the sample.

The activation process can be divided into physical, chemical and physiochemical activation. The physical activation was carried out using CO_2 or steam as activating agent. CO_2 or steam passes through char at high temperature ($>800^oC$) and gasify the carbon as well as widening the existing pore (Tseng et al., 2006). The chemical activation process occurred when char was impregnated with chemicals such as KOH, NaOH, ZnCl or H_3PO_4 before heating at high temperature ($>600^oC$). In this study, KOH was used as impregnating agent to develop pore in activated carbon. KOH has been reported to be a better activation agent in term of both high surface area, adsorption capacity and narrow pore size distribution (Ahmed and Theydan, 2014).

2.3.2 Agrowaste

Agrowaste is considered cheap, abundantly available and renewable material as precursor for activated carbon production. Especially in tropical countries which are abundant in sources, agricultural by-products are often discarded as waste hence contributing to the increasing of agrowaste. This problem can be overcome by converting the agrowaste into activated carbon. Moreover, the activated carbon produced serves as a useful adsorbent for removal of potentially harmful pollutants. In fact, activated carbon produced from agrowaste was proven applicable with high adsorptivity, considerable mechanical strength and low ash content (Savova et al., 2001). For example, corn cob as low cost lignocellulosic waste was used as activated carbon precursor for removing reactive dye orange 16 (Suteu et al., 2011). Mangrove bark waste from charcoal industry is another precursor which has been discovered useful as adsorbent. It is produced from the production of charcoal, firewood and woodchips in large quantity and found suitable to be used as activated carbon precursor. Different kinds of adsorbents were used for dye removal from aqueous solution such as palm kernel fiber, wood shell and tree leaves. Table 2.2 shows some example of agrowaste based activated carbon.

Table 2.2 Activated carbon prepared from agrowaste

Raw material	**Dye**	**Adsorption capacity (mg/g)**	**Reference**
Oil palm shell	Methylene blue	243.9	(Tan et al., 2007)
Posidonia oceanic L.	Methylene blue	285.7	(Dural et al., 2011)
Saw dust	Remazol brilliant violet 5R	453.0	(Vijayaraghavan et al., 2009)
Phragmites australis	Methyl violet	46.9	(Chen et al., 2010)
Cocoa pod husk	Remazol brilliant violet 5R	36.2	(Bello et al., 2012)
Cocoa pod husk	Remazol black B	22.1	(Bello et al., 2011)
Coffee husk	Remazol brilliant orange 3R	71.2	(Ahmad and Rahman, 2011)
Rambutan peel	Malachite green	404.5	(Ahmad and Rahman, 2011)
Sugarcane bagasse	Methylene blue	478.5	(Guimarães Gusmão et al., 2012)
Brazillian pine-fruit shell	Methylene blue	252.0	(Royer et al., 2009)
Pine-fruit shell	Methylene blue	529.0	(Royer et al., 2009)
Tea waste	Methylene blue	85.2	(Uddin et al., 2009)
Wheat straw	Methylene blue	312.5	(Gong et al., 2008)

2.3.3 Peanut shell

Peanut (*Arachis hypogaea L.*) is a popular crop mainly grown as an intercrop in Malaysia, China, India, United States, Nigeria, Indonesia and Myanmar. From statistics presented by Cnagri, the total world peanut production reaches nearly 38 million tons from year 2011 to 2012. Peanuts are used in peanut butter, peanut oil, candies and peanut powder production. However, rising of peanut production has increased the amount of peanut shell (Plate 2.1 (a)) as waste. Peanut shell was tossed after peanut was obtained before dumped at the site. Peanut shell was found having high carbon content (>15%) which was suitable for activated carbon production.

2.3.4 Coconut peduncle

It was reported that the world production of coconut reaches around 64 million tons in year 2009 and still growing based on Coconut Development Authority (CDA). Coconut is known for its useful different part of the tree. Coconut become part of the daily diets of many people because of the oil and milk derived from it were used in cooking. Coconut oil was widely used in soap and cosmetic production. However, the increasing of coconut production leads to increase in generation of waste particularly coconut peduncle. Coconut peduncle (Plate 2.1 (b)) is often thrown away as waste because of its low usability. High carbon content (>15%) in coconut peduncle is one of the reasons why it is suitable as a precursor for activated carbon production while reducing the amount of waste generation.

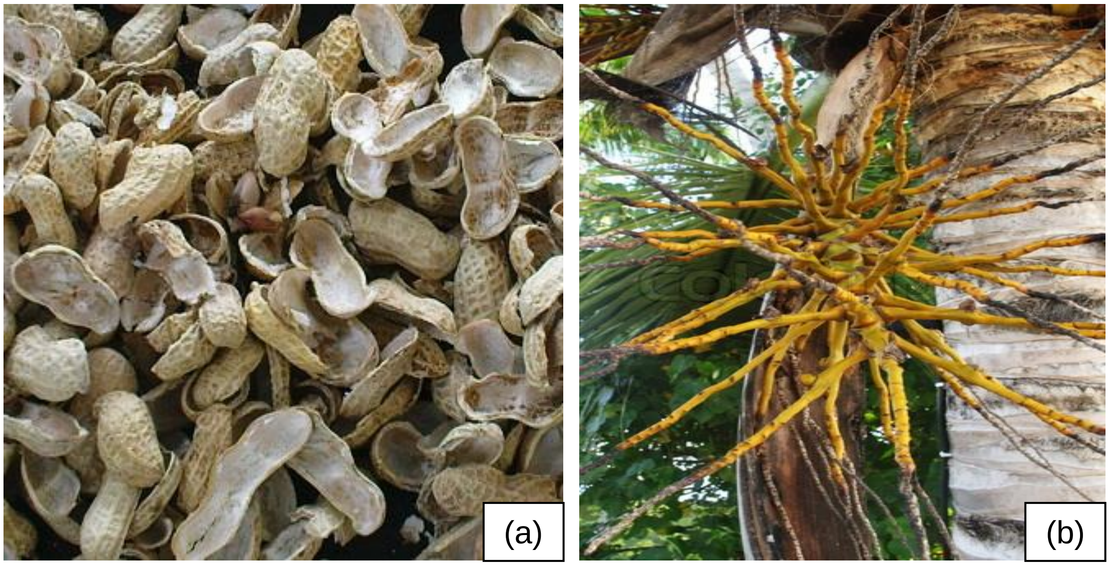

Plate 2.1 (a) Peanut shell; (b) coconut peduncle

2.4 Optimization of operating parameters

2.4.1 Response surface methodology (RSM)

Response surface methodology method (RSM) was used in determining the optimum operating conditions to maximize the effectiveness of activated carbon prepared. It collects various quantitative data from experiments in order to solve multivariate equations and obtain the optimal response. RSM is a collection of mathematical statistical techniques that are useful for the modeling and the analysis problems in which a response is influenced by several variables of factors, and the objective is to optimize this response. The operating factors are assumed continuous and controllable with negligible error whereas the response is assumed to be a random variable (Myers et al., 2009). Statistical technique from RSM has been used by many researchers in experimental design due to its applicability to determine the equations of regression model under certain operating conditions (Dutta et al., 2011). The first step in RSM is to find a suitable approximation for the true functional relationship between response and the set of factors because the relationship between the factors and responses are unknown. Thus, if the response is well modelled by linear function of the factors, then the approximating function is the first order model whereas if there is curvature in the optimum region, then polynomial of higher degree such as the second order model must be used.

2.4.2 Central composite rotatable design (CCRD)

Central composite rotatable design (CCRD) was chosen to obtain response surface due to its reliable, robustness and flexibility. This type of design contains of fractional factorial design with centre points that is augmented with a group of axial points that allow estimation of curvature. The replicates of centre points provide a measure of pure error and stabilize the variance of the predicted response (Ferreira et al., 2007). Generally, CCD consists of 2^n factorial points, $2n$ axial points and n_c centre run, where n represents the number of factors or variables involved in the studies. Distance α of the axial points from the design centre and the number of centre points n_c must be specified in CCD (Myers et al., 2009). CCD is based on the number of factors, n in the design because the value α is the square root of n. The values of α depends on the region of region of interest where the value of the axial distance generally varies from 1 up to α. The axial points are placed on the surface of the cube or hypercube, the latter, resulting in all points being placed on a common sphere. If the distance from the centre of the design space to a factorial point (2n) is ± 1 unit for each factor, the distance from the centre of the design space to axial point is ± α with [α] > 1.

2.4.3 Analysis of data

For data analysis, polynomial model was used for response surface approximation where it represents the functional form of a response surface. Optimal response for the multiple effects of the factors involved is represented as Equation 2.1:

$$Y = b_o + \sum_{i=1}^{n} b_{ii}\, x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \qquad (2.1)$$

where Y is the predicted response, b_o is a constant coefficient-experimental error, b_{ii} is the quadratic coefficients, and bij is the interaction coefficients while x_i and x_j are the coded values of the factors considered.

Then, the analysis of variance (ANOVA) for the data was done by the software in order to confirm the adequacy of the regression model. The statistical properties of the regression model were diagnosed in order to validate the model. Graphs for each model such as contours and 3D graphs were generated for interpretation. Finally, the optimization was done by numerical tools provided in the software packages where optimum conditions for activated carbon preparation were determined.

2.5 Adsorption isotherm

Adsorption is usually described through isotherms, which is the plot of adsorbate amount on the adsorbent with its concentration. Adsorption isotherm can describe the interaction between adsorbent and adsorbate at equilibrium. Adsorption isotherms also express the surface properties and capacities of adsorbent. Isotherm models that are commonly used are Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms.

2.5.1 Langmuir isotherm

Langmuir isotherm model is used for the sorption of molecules to the surface of solid sorbent. It is based on the assumption that the adsorption occur in monolayer nature where the adsorption takes place at specific homogeneous sites within the adsorbent surface. There is no further adsorption can take place at that site once the dye molecule occupies the active site (Hameed, 2009).

The linearized equation of Langmuir isotherm is shown as below:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{2.2}$$

A graph of plot of C_e/q_e against C_e, gives the adsorption coefficient by the slope and intercept of the straight line. The graph plot should show a straight line with the slope of $1/q_m$ and intercept of $1/K_L q_m$. The essential characteristic of the Langmuir isotherm is that it could show a dimensionless constant which expressed by means of R_L. The expression of R_L is as follows:

$$R_L = \frac{1}{1+ K_L C_o} \tag{2.3}$$

where the nature of adsorption processes is unfavourable if R_L higher than 1. The adsorption is linear when R_L equals to unity. The adsorption is favourable when R_L is in the range of 0 to 1. The adsorption process is irreversible when R_L is close to zero.

2.5.2 Freundlich isotherm

Freundlich isotherm is an empirical equation assuming a multilayer adsorption where the adsorption takes place on a heterogeneous surface (Freundlich, 1906). Linearized Freundlich isotherm can be express as:

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \tag{2.4}$$

Freundlich adsorption constant K_F is the adsorption capacity of the adsorbent which represents the quantity of dye adsorbed onto adsorbent for a unit equilibrium concentration. On the other hand, the constant $1/n_F$ in range from 0 to 1 showed whether the adsorption intensity or surface heterogeneity. It becomes more heterogeneous as it gets closer to zero (Haghseresht and Lu, 1998). A value for $1/n_F$ above one is indicative of cooperative adsorption while $1/n_F$ below one indicates a normal Langmuir isotherm (Fytianos et al., 2000). The values for Freundlich constant K_F and $1/n_F$ were calculated from the slope of ln q_e versus ln $c_{e.}$

2.5.3 Temkin isotherm

Temkin isotherm takes into account the effect of adsorbate-adsorbate interaction on adsorption. It proposes that the heat of adsorption of all the molecules in the layer would decrease linearly with the coverage due to these interactions (Temkin and Pyzhev, 1940). The adsorption is characterized by a uniform distribution of binding energies. The linearized Temkin isotherm equation can be expressed as:

$$\mathrm{q_e} = \mathrm{Bln}\mathrm{A}_{T} + \mathrm{BlnC_e} \qquad (2.5)$$

A graph of plot of q_e versus ln C_e yield B which is the constant related to the heat of adsorption and equilibrium binding constant, A_t (l/g).

2.5.4 Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich isotherm is used to estimate the characteristic porosity of the adsorbent and the apparent energy of adsorption. It can be expressed as:

$$\mathrm{q_e} = \mathrm{q_{DR}} \exp(-\mathrm{B_{DR}}\varepsilon^2) \qquad (2.6)$$

Where ε can be correlated to the Polanyi potential (J/mol) by using equation below:

$$\varepsilon = \mathrm{RTln}\left[1 + \frac{1}{\mathrm{C_e}}\right] \qquad (2.7)$$

Free energy, E of sorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution can be calculated from the constant B_{DR} by using Equation 2.8:

$$\mathrm{E} = \frac{1}{\sqrt{2\mathrm{B_{DR}}}} \qquad (2.8)$$

The constant B_{DR} gives the mean free energy of sorption per mole of the adsorbate as it migrates to the surface of the adsorbent from an infinite distance in the solution. The q_{DR} is the maximum adsorption capacity. Both constant B_{DR} and q_{DR} can be calculated from the slope and intercepts of ln q_e versus ε^2.

2.6 Adsorption kinetics

Adsorption kinetic is important to express the rate of adsorption of adsorbate onto the surface of adsorbent. It determines how sorption rates depend on the concentrations of adsorbate and sorption capacity (Ofomaja and Ho, 2007). Adsorption kinetic is important in most of the chemical process as it predicts the adsorbate uptake rate. Several models have been established such as pseudo-first-order and pseudo-second-order kinetic models.

2.6.1 Pseudo-first-order model

Pseudo-first-order model can be expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{2.9}$$

For boundary layer condition, from t = 0 to t = t and q_t = 0 to q_t = t. a linear equation can be obtained by integrating the equation as below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2.10}$$

The values of q_e and k_1 can be determined from the slope and intercept, respectively from the plot of ln (q_e – q_t) versus t. The value of k_1 shows the rate constant for first-order kinetic model. Pseudo-first-order kinetic model is based on the assumption that the rate of adsorption is proportional to the number of unoccupied sites.

2.6.2 Pseudo-second-order model

Pseudo-second-order model (Ho and McKay, 1998) predicts the rate-controlling step is the chemisorption mechanism which was based on the sorption capacity onto the solid phase. Pseudo-second-order model can be expressed by:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{2.11}$$

Equation (2.16) can be rearranged and yields:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 t \tag{2.12}$$

For boundary layer condition, from t = 0 to t = t and $q_t = 0$ to $q_t = t$, a linear equation can be obtained by integrating the equation as shown below.

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \tag{2.13}$$

The value of constant q_e and k_2 can be determined from slope and intercept, respectively from the plot of $\frac{t}{q_t}$ versus t where k_2 is the rate constant of pseudo-second-order model. The rate of pseudo-second-order is dependent on the amount of solute adsorbed on the surface of adsorbent and the amount adsorbed at equilibrium condition.

2.7 Intraparticle diffusion model

Adsorption process is a process that consists of series of steps involving transport of solute molecules from aqueous phase to the surface of the solid particles. Then the process is followed by the diffusion of the solute molecules into the interior part of the pores which is called the rate limiting step because its possibility to be slow process (Santhi et al., 2010). The uptake of the adsorbate varies with the square root of time if intra-particle diffusion is the controlling factor. Intraparticle diffusion model is shown as:

$$q_t = K_{dif} t^{1/2} + C \tag{2.14}$$

where K_{dif}, the rate parameter obtained from the slope of the straight line of q_t versus $t^{1/2}$ and C, intercept of the straight line represent the effect of boundary layer where the larger the value of C, the greater the contribution of the surface sorption in the rate controlling step. If intraparticle diffusion occurs, the plot of q_t versus $t^{1/2}$ should be linear. The rate limiting process is only due to the intraparticle diffusion if the plot passes through the origin. Otherwise, some other mechanism along with intraparticle diffusion is also involved. The following steps are commonly considered to be involved in the mechanism of adsorption (Cheung et al., 2007):

(i) Film diffusion step, where the mass transfer across the external boundary layer film of liquid surrounding the outside of the particle.

(ii) Particle diffusion step, this step is assumed to be very rapid as it describe the gradual adsorption stage whereby the intraparticle diffusion is the rate limiting.

(iii) Diffusion of the adsorbate molecules to the adsorption site, either by pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism.

2.8 Adsorption thermodynamics

Thermodynamic study can evaluate the feasibility of the physiochemical adsorptive reaction (Li et al., 2005). There are three main parameters that must be taken into consideration which are the enthalpy of adsorption (ΔH°), the entropy change (ΔS°) and free energy (ΔG°) owing to the transfer of solute from solution onto the solid-liquid interface (Tan et al., 2008a).

The value of ΔH° and ΔS° is calculated by using the following equation(Sankaran and Anirudhan, 1999):

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (2.15)$$

By plotting a graph of ln k_L versus 1/T, both ΔH° and ΔS° values can be calculated from the slope and intercept of the graph.

Standard Gibbs energy, ΔG° can be calculated relation expressed below:

$$\Delta G^\circ = RT\ln K_L \qquad (2.16)$$

If the overall free energy changes are negative for an adsorption process, the process is said to be spontaneous or vice versa (Özcan et al., 2006). On the other hand, the positive value for standard enthalpy changes, ΔH° shows that the adsorption process is endothermic while negative value show it is an exothermic process. For standard entropy changes, ΔS°, the positive value show the increment of randomness at the solid/solution interface take place in the internal structure of the adsorption and vice versa.

To further evaluate the activation energy of adsorption, Arrhenius equation was applied representing the minimum energy that reactant must have for the reaction to proceed. The Arrhenius equation is shown as below:

$$lnk_2 = \ln A - \frac{E_a}{RT} \qquad (2.17)$$

The values of Arrhenius activation energy of adsorption, E_a and activation factor, A can be calculated from the slope and intercept from plot of ln k_2 versus 1/T where the value k_2 is the average value of rate constant from pseudo-second-order kinetic model.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Peanut shell (PS) and coconut peduncle (CP) were obtained from the Thong Thye Factory Sdn Bhd, Sungai Siput, Perak and local market in Parit Buntar, Perak, respectively. Hydrochloric acid, HCl (37% v/v) and pottasium hydroxide, KOH pellets (85% purity) were obtained from Merck, Germany. Methylene blue (MB) and remazol brilliant blue R (RBBR) were supplied by Sigma-Aldrich (M) Sdn. Bhd. The properties for MB and RBBR were presented in Tables 3.1 and 3.2, respectively. Technical nitrogen, N_2 (purity 99.98) and technical carbon dioxide, CO_2 (purity 99.8) supplied by MOX Gases Sdn. Bhd were used as purging gas to create inert atmosphere and physical activating agent, respectively.

Table 3.1 Properties of MB

Properties	
Dye name	Methylene blue
Molecular formula	$C_{16}H_{18}N_3SCl$
Molecular weight, g/mol	319.85
CAS no.	61-73-4
λ max.(nm)	663
Chemical structure