Modeling of Residual Removal from Palm Oil Mill Effluent by *Ceiba Pentandra*

by

Mohd Zulkefli Bin Mohamad Jamaluddin

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

MAY 2013

Universiti Teknologi PETRONAS
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Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

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(Associate Professor Dr. Mohd Azmuddin Bin Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done unspecified sources or persons.

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MOHD ZULKEFLI BIN MOHAMAD JAMALUDDIN

ABSTRACT

This research will explore and incorporate the values and reactions of *Ceiba Pentandra* as a medium for residual oil removal from the palm oil mill effluent (POME). The behavior and characteristics of *Ceiba Pentandra* in oil adsorption is tested in experimental laboratory. To understand the characteristics and capabilities of *Ceiba Pentandra* for residual oil removal, modeling will be developed as a means of evaluating the prediction value with experimental data. The models are tested and elucidated using adsorption kinetics and adsorption equilibrium isotherms. From the results of these models, capacity and oil absorption capacity *Ceiba Pentandra* will be proved to have a significant value as one of the efficient and eco-friendly agent in oil removal.

ACKNOWLEDGEMENTS

I would like to thank God for providing all the needs to accomplish this research. Also, I would like to express my sincere appreciation to my supervisor, Assoc. Prof. Mohd Azmuddin Bin Abdullah for his valuable suggestions, comments, patience and trust during this work.

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ABBREVIATIONS AND NOMENCLATURE

Department of Environment	: DOE
Dubinin-Radushkevich isotherm	: D-R
Palm oil mill effluent	: POME
Regression squared	: r^2
Scanning electron microscopy	: SEM

CHAPTER 1

INTRODUCTION

1.1. BACKGROUND STUDY

Removing of oil from wastewater has been a study of concern for environmentalist. One of such wastewater is palm oil mill effluent (POME). Even though the composition of oil inside POME about 0.5% to 2%, it still a pollutant that may bring harmful to environment as well as human [1,2]. Oil does not dissolve in water. It will form a layer on the surface that prevents light and oxygen for aquatic organisms [2]. In a case of larger or huge quantity of oil involved such as oil spills, the effect can be catastrophic [3]

There are many ways or treatment in removing the oil from wastewater. There are conventional physical applications and chemical or sorbent aids. Floatation, one of the physical applications, separating low-density oil and grease from a liquid phase, through introduction of air bubbles into the liquid phase. Other than floatation, oil-skimmer, corrugated plate interceptor and API (American Petroleum Institute) Separator also widely being used.

The usage of chemical aids or sorbent is divided into synthetic and natural substances. Synthetic usually made up from cationic, anionic and non-anionic substances as well as alum or iron salt. While, natural substances infamously derived from the extraction of brown seaweeds; sodium alginate, and chitosan which extracted from the shells of shrimp and other sea crustaceans [4].

Most of the popular treatments used sorbents which involved sorption processes. These sorbents just not only capable in oil removal but also have ability to remove any substances which have affinity toward physical adsorption and chemisorptions [5]. The usage of sorbents as oil sorption gives advantages economically [6]. And organic sorbents, which is natural, proved to be more feasible price from inorganic or synthetic. One of this sorbents, that being tested in this project, is *Ceiba Pentandra* (L.) Gaertn.

Ceiba Pentandra or kapok or locally known in Malaysia as kekabu. It widely cultivated in Southeast Asia as well as other parts in East Asia and Africa [7]. Its fibers have the tendency and capacity for oil sorption.

In this study, the aim is to investigate and explore the adsorption capability of *Ceiba Pentandra* in residual oil removal from POME. The adsorption process, generally, is an application of separation of a substance or adsorbate from a phase, which then followed by accumulation of it into adsorbing material, or adsorbent [8]. *Ceiba Pentandra* ability of adsorption depends of its attributes.

After being tested in experimental ways, the oil sorption data for *Ceiba Pentandra* is used to elucidate its kinetics behaviour using various kinetics models: Pseudo-first-order, Pseudo-second-order, Bangham's equation and intra-particle diffusion model [9]. To analyze the equilibrium study for the performance of *Ceiba Petandra*, the experimental data is included into adsorption isotherms such as Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich (D-R), Redlich-Peterson (R-P), Radke-Prausnitz and Koble-Corrigon model [9,10].

1.2. PROBLEM STATEMENT

The capacity for residual oil removal of *Ceiba Pentandra* or kapok has correlations with its experimental data and information regarding the process of oil sorption. Therefore, using the adsorption kinetic equation and adsorption equilibrium isotherm equations, models of performance are going to be built to determine the best-fit and

effectiveness feature of *Ceiba Pentandra* as the adsorbent. The result will lead to the optimum exercises of *Ceiba Pentandra* in actual and mass application.

1.3. OBJECTIVES

a. To elucidate the reactions and processes involved in the residual oil removal by *Ceiba Pentandra* based on the packing density factor.

b. To develop the model for the reaction process (using adsorption kinetics and adsorption equilibrium isotherms)

c. To perform simulation using EXCEL and/or MATLAB from the result of the reaction process.

1.4. SCOPE OF STUDY

This research focuses to investigate the performance of *Ceiba Pentandra's* oil sorption in residual oil removal. The study comprehends:

- The characteristics of *Ceiba Pentandra* (hydrophobic, oleophilic, oil selectivity, oil sorption capacity) which related to its performance.
- The adsorption kinetic models and their explanation toward mechanism of oil sorption.
- Adsorption isotherm models and their explanation to configurate the adsorption equilibrium of *Ceiba Pentandra's* performance.

CHAPTER 2

LITERATURE REVIEW

2.1. OILY WASTEWATER: PALM OIL MILL EFFLUENT

Palm oil industry in Malaysia is known for the second largest in the world behind Indonesia. For the latest January, 1.6 million tonnes of crude palm oil was produced with increasing of 2.1% from 1.3 million tonnes in January 2012. As the production of crude palm oil become large, the amount of palm oil mill effluent (POME) also will be larger. Nevertheless, palm oil mill industry contributed as one of the most polluting industry in Malaysia. The fact is, about 44 million tonnes of palm oil mill effluent was generated in the year of 2008. An estimation about 2.5-3.5 tonnes of POME is generated for every tonnes of crude palm oil than being produced [15].

The effluent of palm oil mill or palm oil mill effluent (POME) is known as high strength wastewater. It is a brownish colloidal suspension and contains high concentration of COD, BOD, total solids (TS), suspended solids (SS) as well as oil and grease. It is also a non-toxic compounds as due to the involvement of chemicals during the process of oil extraction. However, POME cannot be discharged directly to the environment; it has to be treated onto standard level implemented by Department of Environment (DOE).

There is about 4000 mg/L of oil and grease inside a standard discharge of POME. When the amount of oil and grease is measured alone for each individual waste water stream, the sterilizer, oil clarification and hydro cyclone, the value varies to 4000

mg/L, 7000 mg/L and 300 mg/L respectively. DOE then has set the regulatory limit to 50 mg/L under the Environmental Quality (prescribed Premises) (Crude Palm Oil) Regulations 1977, promulgated under the powers of Section 51 of the EQA to control the discharge value [16].

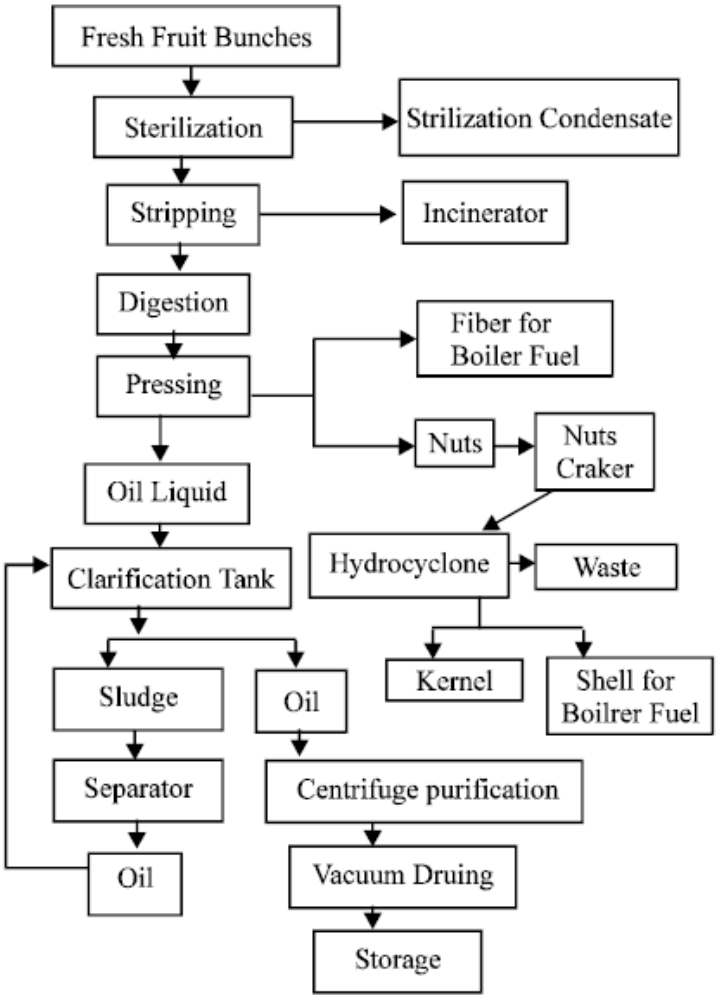


FIGURE 2.1.: A process flow and block diagram for atypical palm oil milling

The generation of POME resulted from various point during palm oil processing. These points are:

- Fruit washing.
- Sterilization condensates.

- Clarification sludge.
- Centrifuge purification and vacuum drying.
- Hydro cyclone drain-off.
- Various boiler blows down, tank and decanters.

The discharges of oil mainly came from sterilization, clarification sludge, centrifuge purification, vacuum drying and hydro cyclone processes. In sterilization process, the fresh fruit bunches are heated with high pressure steam (120-140^{o}C at 40psi) with a minimal delay. This process causes the oil hydrolysis and fruit deterioration by inactive the lipolytic enzymes. In clarification sludge, the sludge undergoes oil recovery which to retrieved back any oil that accumulated inside the sludge bulk. While the process of water removal and drying is applied in centrifuge clarification, vacuum drying and hydro cyclone [1]. The oil inside the POME usually recovered using physical process. The process called oil trap used physical barrier or baffles that skim the oil that float atop, and implemented as the first process in POME waste water treatment.

2.2. *Ceiba Pentandra*

FIGURE 2.2.: Young *Ceiba Pentandra* or kapok fruit (left) and matured fruit (right).

Ceiba Pentandra or kapok belong to Bombaceae family. It widely planted in Malaysia as well as Southeast Asia either traditionally or grows naturally. Mature tree will bears hundreds of pops of fruit, up to 15 cm long which filled with fibrous seeds. Young fruits are green in colour and mature fruits usually in yellowish-brown as shown by Figure 2. During maturity, the fruits' skin usually naturally 'popped' or 'open' although still on the tree. Its seeds can be processed into oil for soap manufacturing. The residue can be used as fertilizer or livestock feed. In region of Nusantara, *Ceiba Pentandra* is used as packing materials for pillow and cushion. The leaves of *Ceiba Pentandra* tree have medicinal values for the Chinese, and the trunk has ability as resources for pulp material in papermaking [12].

These fruit exhibited excellent buoyancy. It is hydrophobic, moist-resistant and does not wet with water. This due to the air channel that entrapped inside the fiber thus prevents water entrance. Due to the attributes also *Ceiba Pentandra* has capacity and high selectivity for oil sorption or oeleophilic. The waxy surface also contributes to the selectivity of oil sorption as well water-repellent agent. Above all, the interfacial

interactions or Van de Waals force explained the high selectivity of *Ceiba Pentandra* towards oil-water mixtures.

Ceiba Pentandra fiber has a hollow structure with large lumen. This shows feature valued *Ceiba Pentandra* as an excellent absorbent for oil. This fiber comprises 64% cellulose, 13% lignin and 23% pentosan [6]. The oil sorption capacity is derived by few others attributes such as availability of voids surface ratio and rod-like structure with similar fineness that provides space for oil entrapment. Higher effective spaces inside the kapok assembly predominantly affect the sorption capacity. The network of hollow structures gives *Ceiba Pentandra* the ample interstitial area for oil to be retained and trapped. By allowing the oil to drip from the test sample for duration of specified time, dynamic oil retention can be calculated. Dynamic oil retention qualified for the parameter for oil sorption capacity.

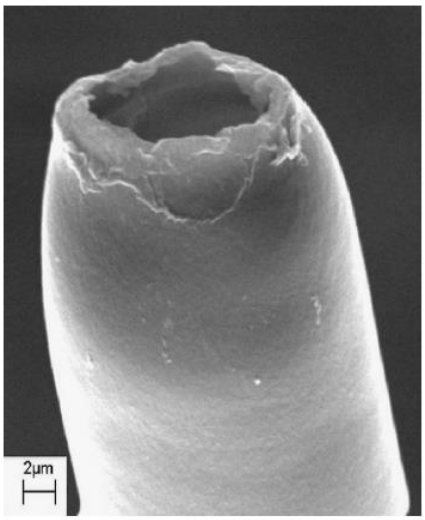


Figure 2.3.: Scanning electron microscopy (SEM) image of *Ceiba Pentandra* showing the hollow structure with large lumen.

Also, sorption capacities of *Ceiba Pentandra* assemblies were dependent on their packing densities. When these assemblies were allowed to drain, they showed high

retention ability for oil. From the researches, during 1 hour of dripping *Ceiba Pentandra* just lost about 8% of absorbed diesel and HD40 (engine oil), and 12% of the absorbed AWS46 (hydraulic oil) from total absorption [6]. From the research, lower packing density reduces the interactions between oil with *Ceiba Pentandra* surface. Hence, it results a faster water breakthrough time. However, lower packing density allows the oil droplet to coalesce, emulsified and becomes large to be trapped inside the *Ceiba Pentandra*. At higher packing density, the liquid flow rate creates premature interactions of the liquid with *Ceiba Pentandra*. Due to that, a lower performance in oil retention is occurred. Higher packing density needs a maintain flow rate of the feed causing the reduction of void porosity and increases the velocity. Even the interaction of forces are weaken, the disperse phase droplets are drive deeper into *Ceiba Pentandra* bed therefore ensures optimum entrainment and more durable during filtration process [8].

Reusability of *Ceiba Pentandra* is evaluates the durability of over prolonged usage. The main criterion is the judging for *Ceiba Pentandra* ability by the number of cycles it can endure before becoming unusable. After the oil is absorbed, by simple squeezing the oil can be removed with the value of efficiency >85%. Nevertheless, more consistent value can be obtained through centrifugation; 97% retrieved from 0.02 g/cm3 absorption and 83% retrieved from 0.09 g/cm3 absorption. From the researched also, *Ceiba Pentandra* is found out can only endures four cycles for reusability. However, the capacity of sorption is decreased to 72% during second cycle. Eventually, the rate is dropped to 70% at fourth cycle [6].

2.3. ADSORPTION KINETIC AND ADSORPTION ISOTHERM MODELS

Adsorption kinetic models explain the chemical reaction rate as well as the factors that affecting the rate of reaction. In adsorption kinetics, the measurement of sorption rate constant is the best way in evaluating the basic qualities that a good adsorbent should have. One of the examples is the time required for an adsorbent to remove the

adsorbate. Pseudo-first and pseudo-second order models are the most common models that being used to explain the adsorption kinetics [8].

The concentration is said to be in equilibrium when the solute remains the same. It is a condition when the net transfer of solute between fluid and adsorbent is zero. Adsorption isotherms describe the relationship of equilibrium between the adsorbate concentration inside the adsorbent as well as in the liquid phase at constant temperature. These models propose the interaction forces in the process; study the mechanisms that involved, the parameters that need to be improved and the adsorption performance. All of them are critical and importance aspects in adsorbent optimum usage. The most applied isotherms are Langmuir and Freundlich which based on thermodynamic equilibrium. These empirical isotherms are known as three-parameter isotherms. Other isotherms models are Redlich-Peterson, and Radke-Prausnitz. There are also four-parameter isotherms. Weber-van Vliet model and Baudu model are belong to this type. And for Fritz-Schlunder model, it is under five-parameter models.

The accurate elucidation of the experimental data is determined by the equilibrium data. Adsorption capacity and the optimum adsorption isotherm parameters can be being estimated using linear least squares and different error analysis equations. However, non-linear method is said to be a better way in obtaining the equilibrium isotherm parameters. Nevertheless, linear regression method is a favourite one. In this error distribution changes, the final result can be either the best of the worst.

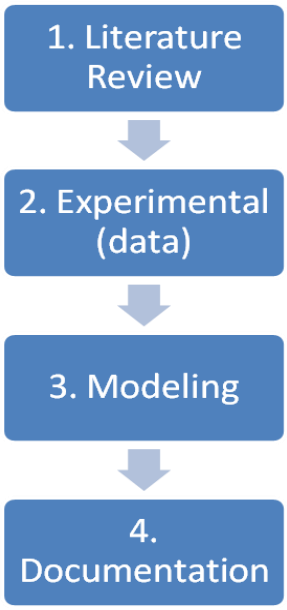
CHAPTER 3

PROJECT WORK

3.1. PROJECT PROCEDURES

The methodology for conducting this research project is waterfall methodology. The project is planned at the very beginning starting at the top with each phase or work activities is stated with fixed deadline following the Gantt chart.

Below is the general research methodology which comprises the work activities throughout the project in order to achieve the result and fulfilled the objectives. There are four general procedures that compromise the overall methodology for this project: *Literature review*, *Experimental* (which is the source of data), *Modeling* (the most important task) and Documentation respectively. In Documentation, the whole research will be documented and detailed properly. Conclusion is derived. The models will be elucidated in term of most favourable (packing density).



FIGUR3 3.1.: Process flow or procedures for the project.

3.1.1. Literature Research

In literature research, we gather as much as possible information from various reliable sources for the purpose of aiding during the beginning as well as throughout the project development. For preliminary search, the keywords used are *Ceiba Pentandra*, palm oil mill effluent (POME), oil sorption, adsorption kinetics and adsorption isotherms.

3.1.2. Experimental (data)

Ceiba Pentandra's adsorption ability is firstly tested in laboratory. For experimental activities, the conducting will be under collaboration and mutual understanding with another student. The recording suitable data is then going to be used to elucidate and design into the kinetic and equilibrium isotherm models.

The experiment conducted the test s based on six different packing density of raw *Ceiba Pentandra*. The packing densities that being tested are: 0.02 g/cm^3, 0.04

g/cm^3, 0.06 g/cm^3, 0.08 g/cm^3, 0.09 g/cm^{3}and 0.1 g/cm^3. These packings contain different capacity in adsorption range. Therefore, from the data, models are elucidated in order to find a favourable packing density that has the optimum value in oil adsorption practicability in the real field.

3.1.3. Modeling

Using the identified values and parameters obtained from the process reaction, models of simulation are developed using suitable application such as MATLAB or EXCEL. These models are based on the adsorption kinetics and adsorption isotherms. The type of adsorption kinetics and adsorption isotherms that being selected as the preliminary equations to be used are as follow:

3.1.3.1. Adsorption Kinetics

Kinetics models are used to investigate the sorption mechanism and potential rate controlling steps. Both of these are useful for selecting the optimum operating conditions for *Ceiba Pentandra* [9]. There are three adsorption kinetic models that are being proposed. These models are as below:

- Pseudo-first-order.
- Pseuso-second-order.
- Intra-particle diffusion model.

The pseudo-first-order rate expression is based on solid sorption capacity. While, pseudo-second-order equation predicts the behaviour of the model over the data range. Same as pseudo-first-order, the second order equation also derived based on oil sorption capacity of the solid phase. The rate controlling step for this kinetic model is chemisorptions [9]. These two models are the most common models and being widely used compare to intra-particle diffusion model.

3.1.3.2. Adsorption Isotherms

Isotherm models are used to describe the adsorption equilibrium. They are associated with the evaluation and correlations for equilibrium curve which to optimize the design of sorption system [9]. The adsorption isotherm models that going to used as follow:

- Langmuir isotherm.
- Freundlich isotherm.
- Tempkin isotherm.
- Dubinin-Raduskevich (D-R) isotherm.

Langmuir isotherm is the simplest theoretical model for monolayer adsorption. It being used originally to develop and represent chemisorptions for a set of identical and localized sites of adsorption [8]. This isotherm assumes that all sites have equal affinity for the adsorbate. While, for Freundlich isotherm, it based on the relationship of equilibrium between heterogeneous surfaces. This isotherm assumes that the adsorption sites are distributed exponentially respected to the adsorption heat. The applicable for Tempkin is used to assume the adsorption heat decreases linearly with the due to the adsorbent-adsorbate interaction. Furthermore, Dubinin-Radushkevich isotherm assumes that the sorption curves characteristics are related to the adsorbent porosity [9].

3.1.3.3. Evaluation of Data

For both adsorption kinetics and adsorption isotherms, the comparisons are going to be modelled and evaluated using linear and non-linear method. The adsorption kinetics and adsorption isotherms will be modelled using the adequate data which being evaluated using R^2 (regression squared). In linear regression, R^2 is the most often being used. R^2 will show of how good the line

of result matches the original. It is a statistical term in on term in determining and predicting another (better or not). The regression correlation coefficient of R^2 is used to determine the linear equation of best fit with the nearest value of R^2 to unity (value of 1.0) is considered the most favourable. When the condition if fall to 0.0, the prediction will falter while when the value of R^2 reaching 1.0, the prediction towards one term from another is better. R^2 can be derived from the graph. R^2 also can be calculated using the formula below:

CHAPTER 4

RESULTS AND DISCUSSION

4.1. ADSORPTION KINETIC MODELS

From the adsorption kinetic, there are three models that have been elucidated. Based from the data gained, the result is as follow:

Pseudo-first-order kinetic is used for the plot of log(q_e-q) versus time (t). Its rate of expression is based on solid sorption capacity. The plotted models are shown in Figure 4.1. Constant k_1 is calculated from the gradient. From the models, packing density 0.02 g/cm^3 shows the lowest r^2 with the value of 0.399. Packing density 0.04 g/cm^3 is second lowest with the value of 0.702. For 0.08 g/cm^3, 0.09 g/cm^3 and 0.10 g/cm^3, the range of r^2 between 0.65 to 0.69. 0.06 packing density shows the highest value with 0.702, the nearest value to 1. Therefore 0.06 g/cm^3 is the favourable condition. The parameters are presented in Table 4.1.

Pseudo-second-order kinetic models are shown in Figure 4.2. Its equation is used to predict the behaviour of the model over the data range. From the plotting of t/q versus t, the gradient of $1/q_e$ is used to calculate the value of q_e. The pseudo-second-order's constant, k_2 is calculated from the y-intercept. From pseudo-second order kinetic models 0.09 g/cm^3 and 0.10 g/cm^3 packing density suggest the sorption following pseudo-second-order adsorption kinetic with value of 0.980 and 0.915 respectively. The parameters are presented in Table 4.2.

Intra-particle apart pseudo-first and second order is also a common technique used to identify the involved mechanism in the process of adsorption. For intra-particle diffusion model as in Figure 4.3., the constant k_d and value of thickness of the boundary layer, I are calculated from the gradient and y-intercept respectively. This kinetic model plots a condition of q versus $t^{1/2}$. Same with pseudo-first-order the value of r^2 that suggest the favourable is between the range of 0.70 to 0.75. Monotony with pseudo-second-order in term of packing density, the packing densities that followed the intra-particle diffusion favourability are 0.09 g/cm^3 and 0.10 g/cm^3 with the 0.10 g/cm^3 is the most favourable. The parameters are presented in Table 4.3.

4.1.1. Pseudo-first-order

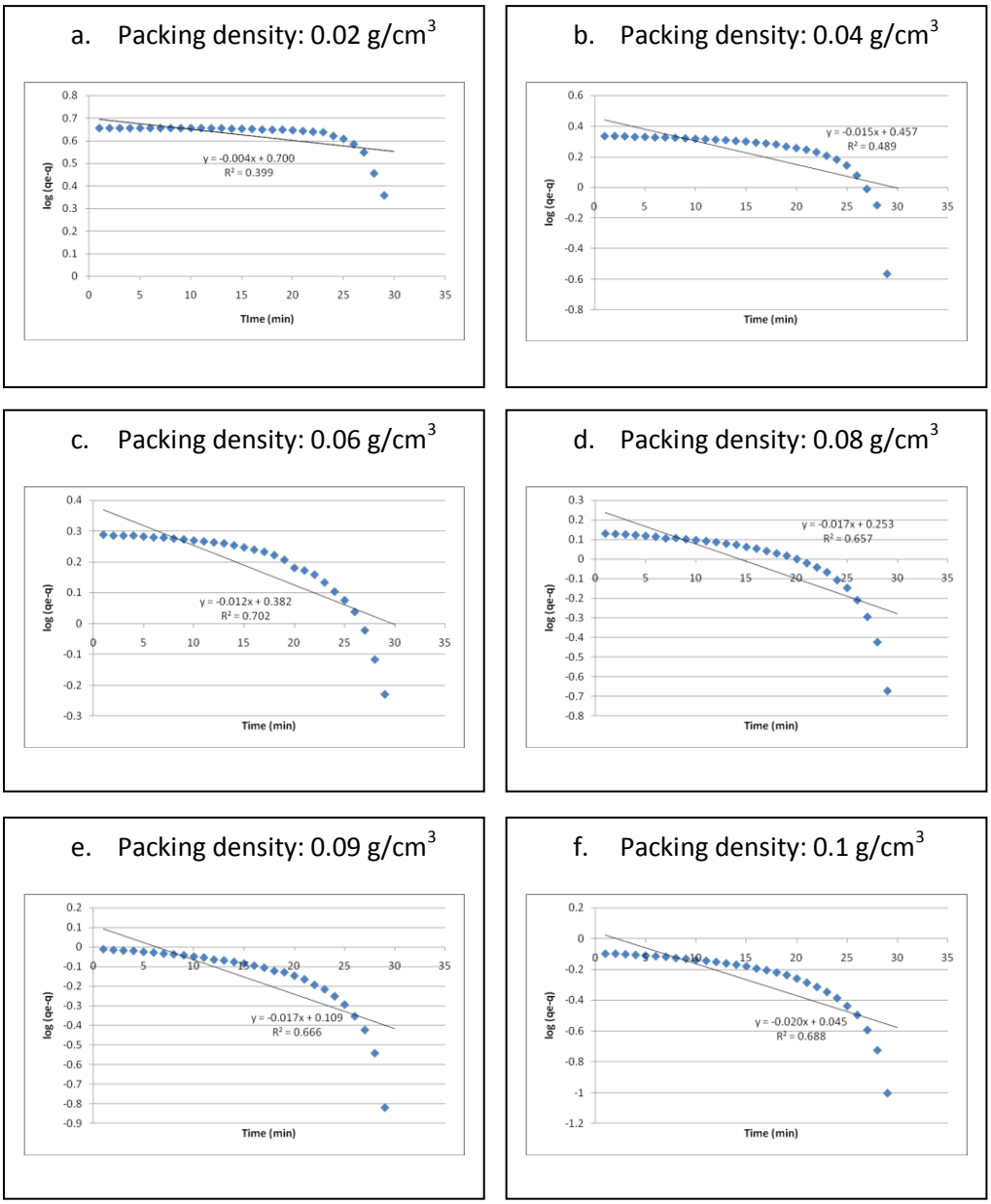


Figure 4.1.: Pseudo-first-order kinetic models

4.1.2. Pseudo-second-order

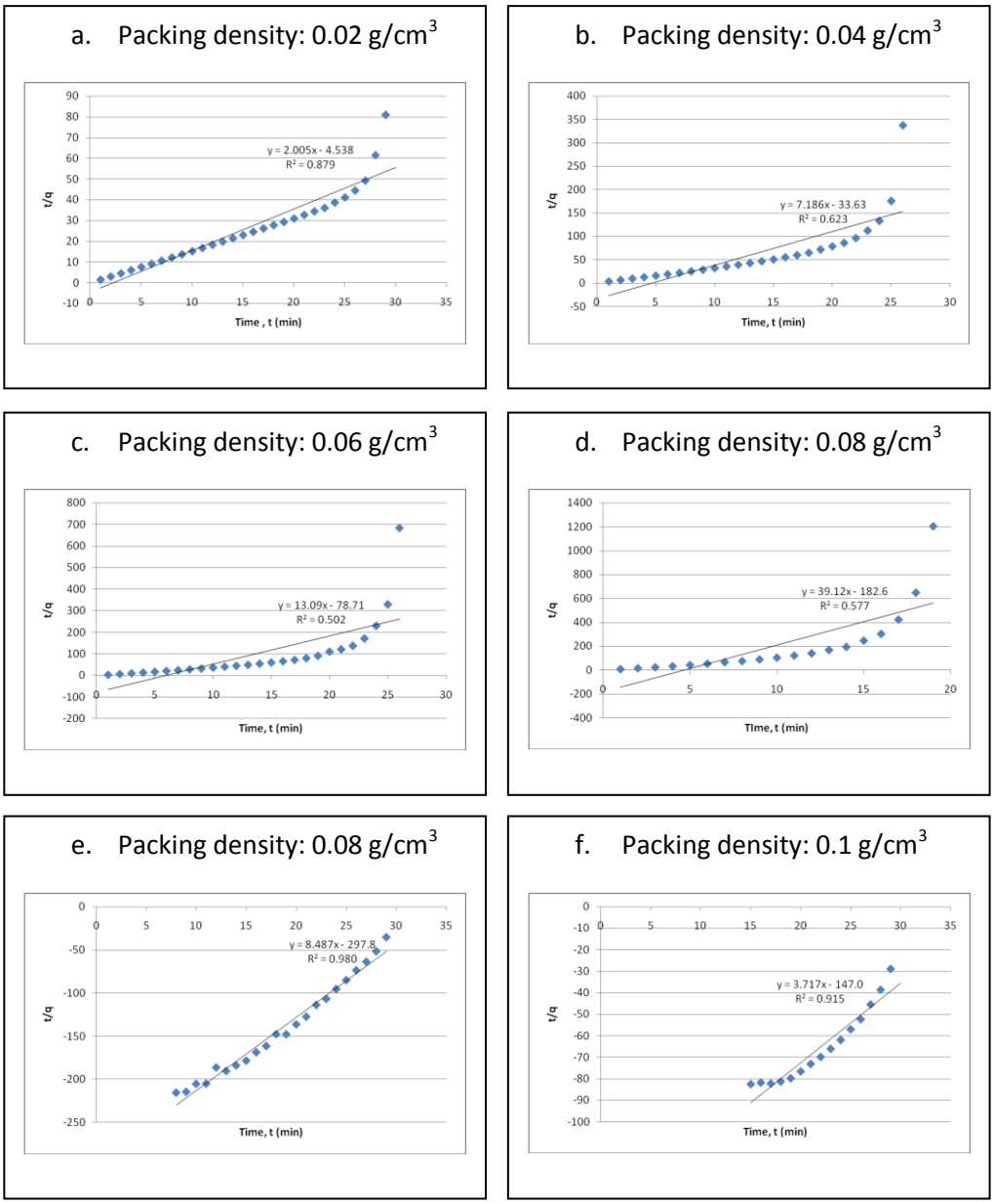


FIGURE 4.2.: Pseudo-second-order kinetic models.

4.1.3. Intra-particle Diffusion Model

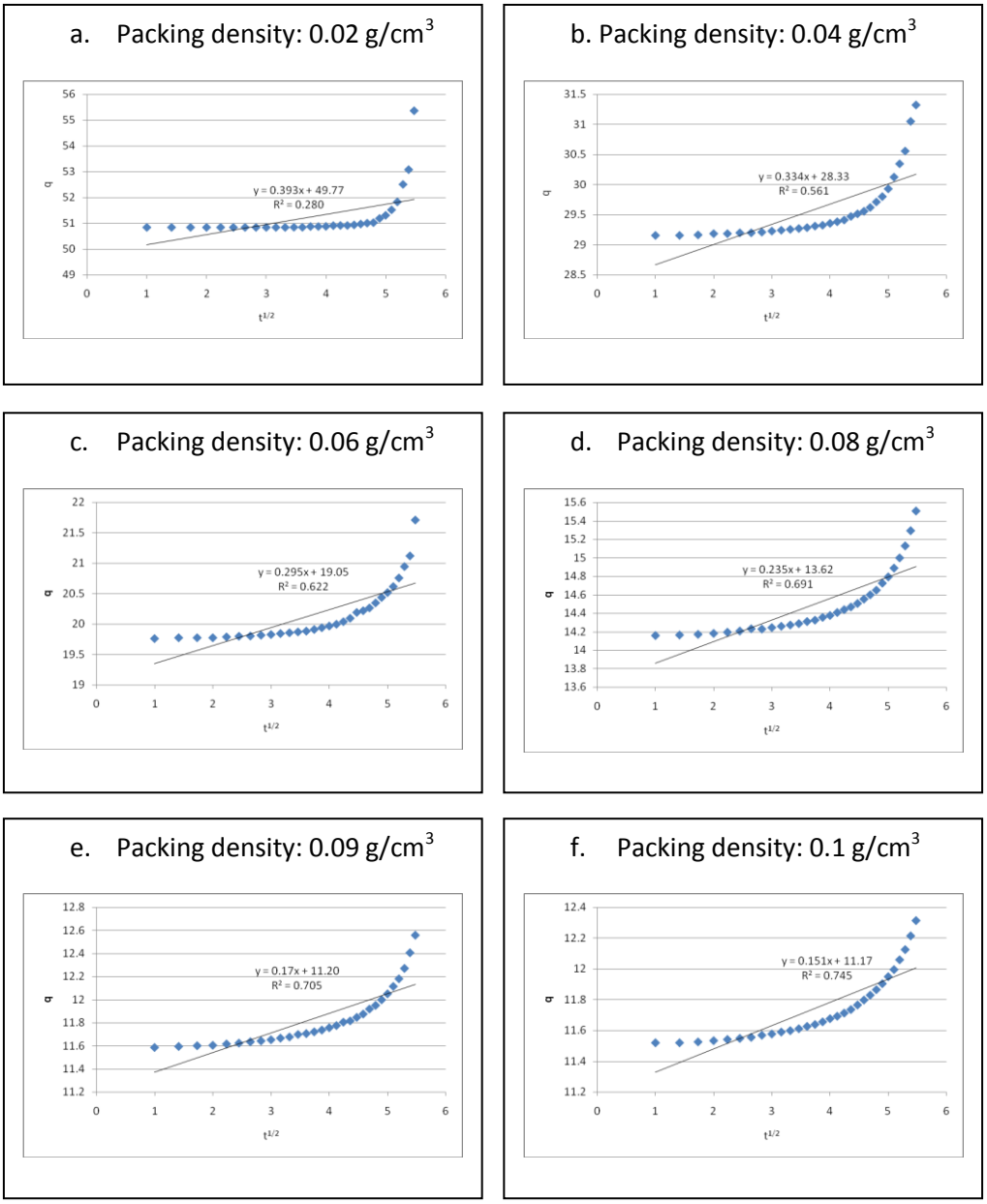


FIGURE 4.3.: Intra-particle diffusion models.

4.1.4. Parameters Tabulation

Packing density (g/cm^3)	**0.02**	**0.04**	**0.06**	**0.08**	**0.09**	**0.10**
q_e **(mg/g)**	55.371	31.32	21.708	15.505	12.56	12.314
k_1 **(min^{-1})**	0.0921	0.0346	0.0276	0.0392	0.0392	0.0461
r^2	0.399	0.489	0.702	0.657	0.666	0.688

TABLE 4.1.: Pseudo-first-order parameters.

Packing density (g/cm^3)	**0.02**	**0.04**	**0.06**	**0.08**	**0.09**	**0.10**
q_e **(mg/g)**	52.632	29.412	19.608	14.085	11.630	11.494
k_2 **(g/mg.min)**	0.0190	0.0340	0.0510	0.0710	0.0860	0.0870
h **(mg/g.min)**	52.632	29.412	19.608	14.085	11.630	11.494
r^2	0.879	0.623	0.502	0.577	0.980	0.915

TABLE 4.2.: Pseudo-second-order parameters.

Packing density (g/cm^3)	**0.02**	**0.04**	**0.06**	**0.08**	**0.09**	**0.10**
K_d **(mg/ $g.min^{1/2}$)**	0.393	0.334	0.295	0.235	0.170	0.151
I **(mg/g)**	49.770	28.330	19.050	13.620	11.200	11.170
r^2	0.280	0.561	0.622	0.691	0.705	0.745

TABLE 4.3.: Intra-particle diffusion parameters.

4.2. ADSORPTION ISOTHERM MODELS

From the adsorption isotherm, four models have been elucidated. Based from the data gained, the result is as follow:

Langmuir isotherm plots C_e/q_e versus C_e models. It assumes that all sites have equal affinity for the adsorbate. The plotted models are shown as in Figure 4.3. Constant k_L and α_L are calculated from the y-intercept and gradient respectively. The r^2 values for all packing densities are in the range of 0.995-0.998, thus suggesting that the sorption followed Langmuir adsorption. The most favourable packing densities will be 0.02 g/cm^3 and 0.10 g/cm^3 with both posses r^2 of 0.998. The parameters are presented in Table 4.4.

Freundich isotherm is shown by models of Figure 4.5. This isotherm assumes that the adsorption sites are distributed exponentially respected to the adsorption heat. The plotting of log q_e versus log C_e will yield the constant $1/n_F$ and k_F. The value of $1/n_F$ indicates the favourability for $0 < 1/n_F < 1$. The value of $1/n_F$ at 0.019-0.045 elucidates the heterogeneity formation on sorbent surfaces. The value of r^2 for Freundlich isotherm that suggest the most favourable condition is packing density of 0.10 g/cm^3 with the value of 0.712. The parameters are presented in Table 4.5.

For Tempkin isotherm, it is used for the plot of q_e versus ln C_e as in Figure 4.6. It assumes the adsorption heat decreases linearly with the due to the adsorbent-adsorbate interaction. The isotherm constant, A and adsorption heat related constant, b are derived from both gradient and y-intercept. b is further derived from constant B using the formula from Appendices. From the models, packing density 0.10 g/cm^3 shows the favourable condition with the highest value of r^2 or the nearest with unity of 1 with the value of 0.705. The parameters are presented in Table 4.6.

Dubinin-Radushkevich (D-R) isotherm assumes the sorption curves characteristics are related with the adsorbent porosity. The models of ln q_e versus ε^2 that have been plotted based to this isotherm are shown in Figure 4.7. ε is the Polanyi potential that can be calculated using the formula in Appendices. The theoretical maximum

capacity of Q_D and D-R constant of B_D are elucidated from the y-intercept and gradient respectively. Packing density of 0.10 g/cm^3 shows the favourability with the value of r^2 of 0.619. The parameters are presented in Table 4.7.

4.2.1. Langmuir Isotherm

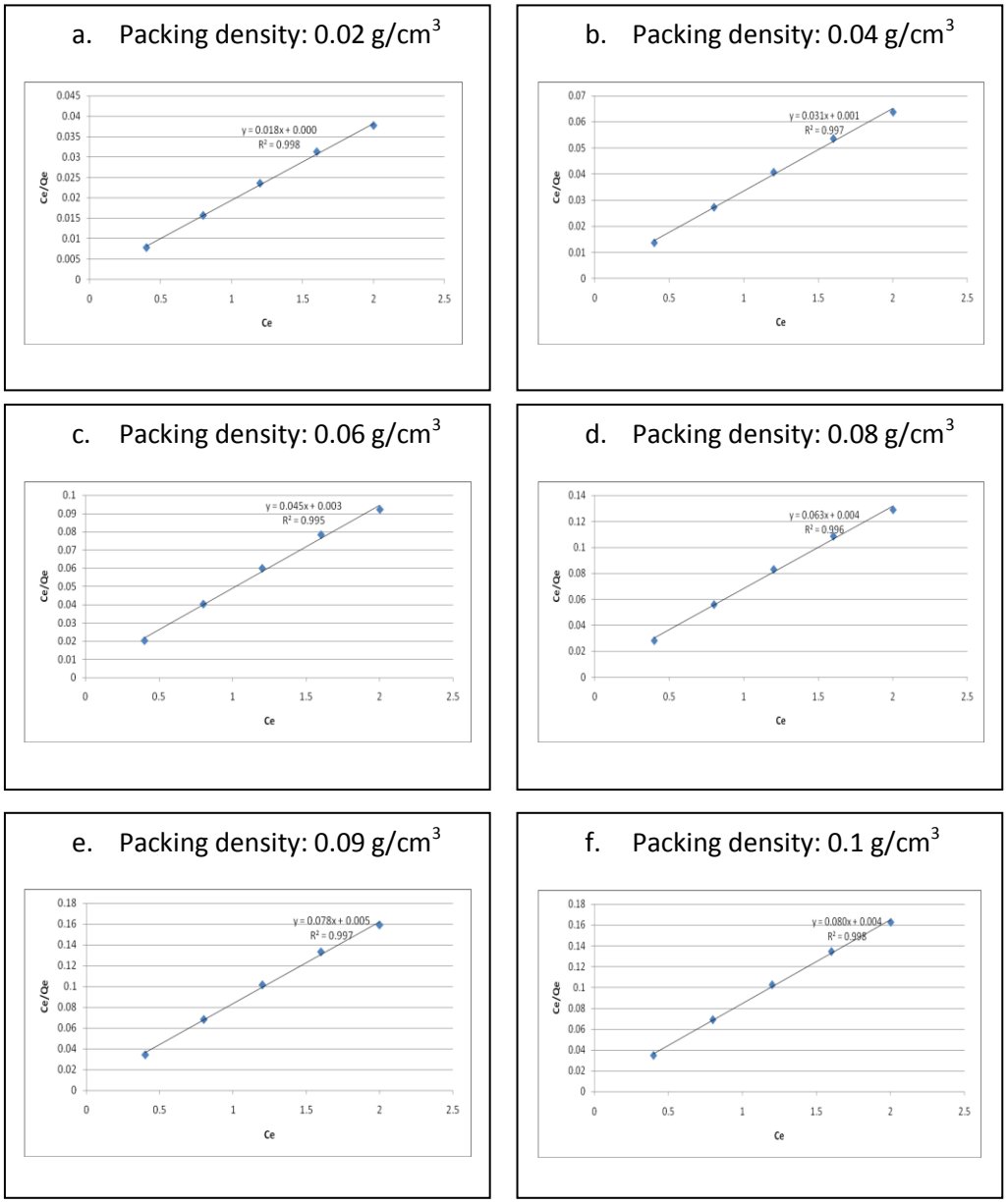


FIGURE 4.4.: Langmuir isotherm models

4.2.2. Freundlich Isotherm

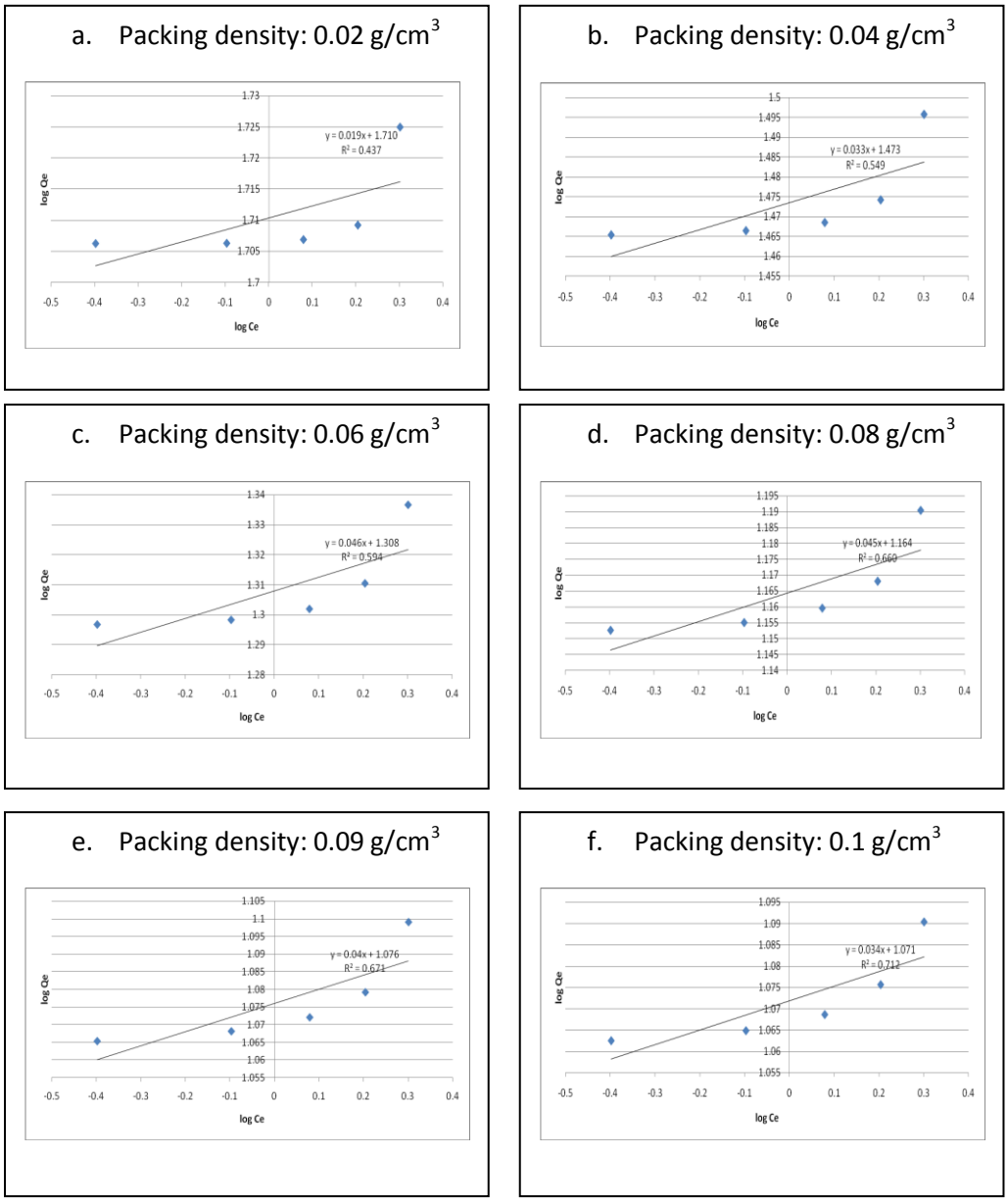


FIGURE 4.5.: Freundlich isotherm models

4.2.3. Tempkin Isotherm

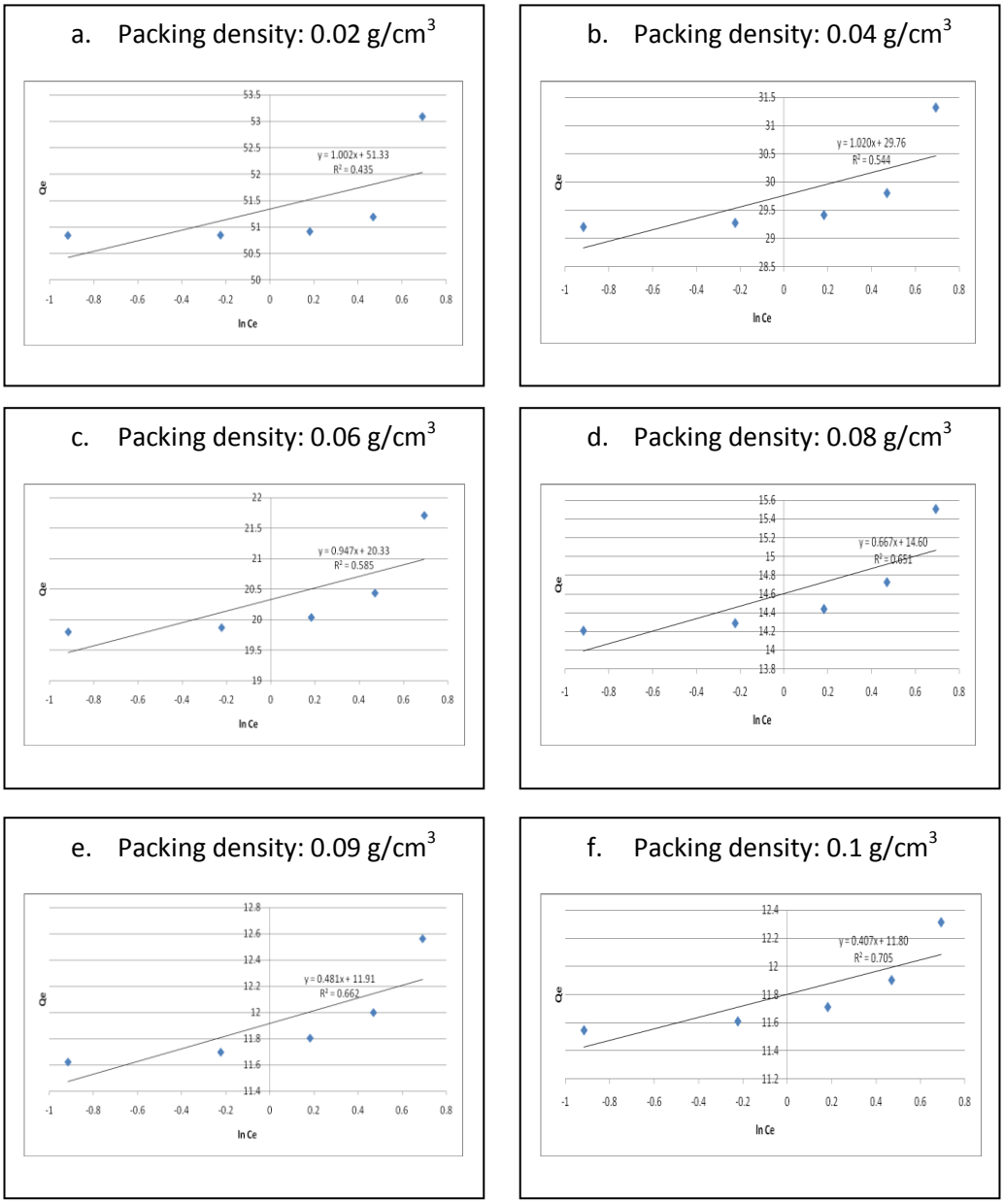


FIGURE 4.6.: Tempkin isotherm models

4.2.4. Dubinin-Radushkevich (D-R) Isotherm

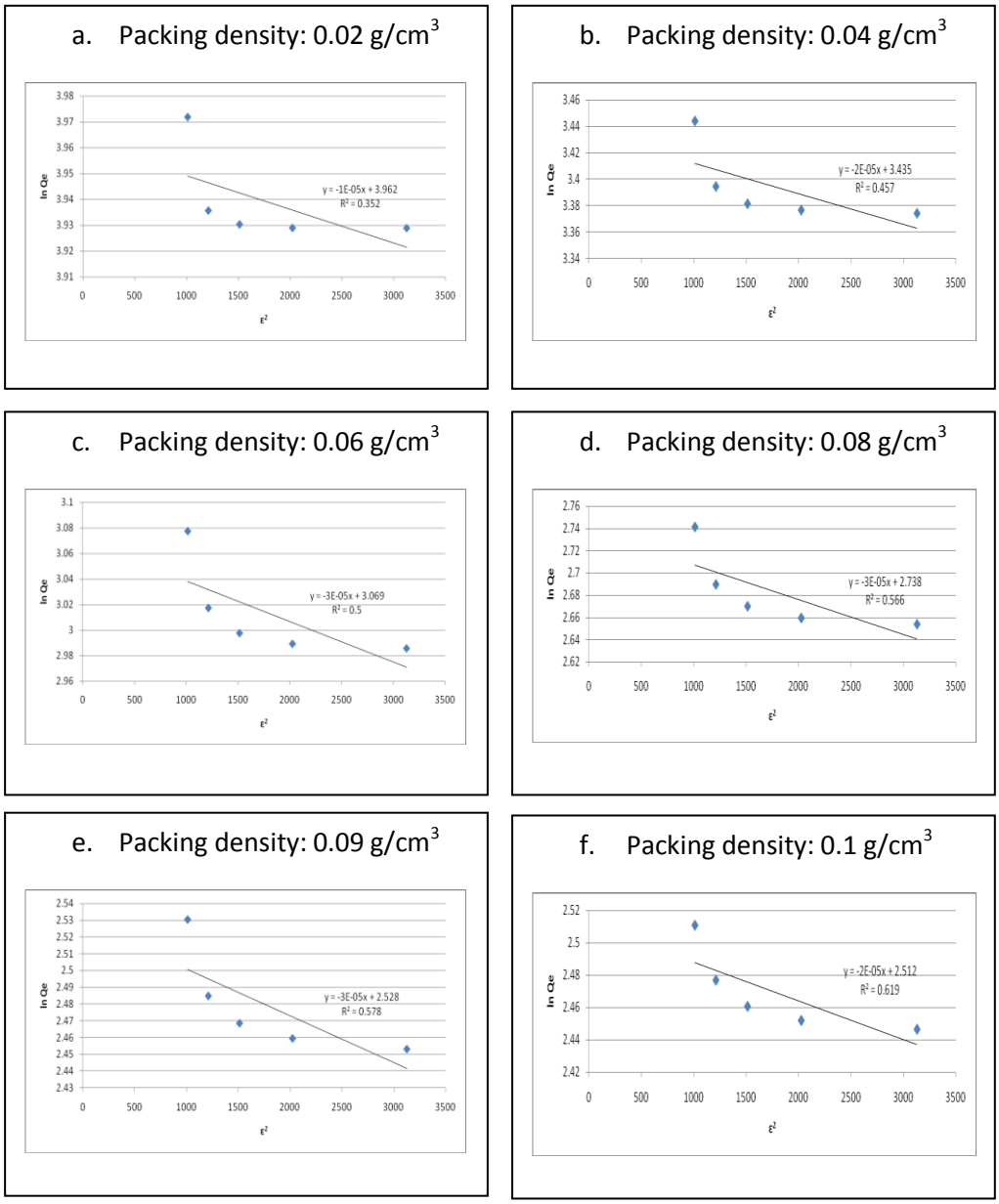


FIGURE 4.7.: Dubinin-Radushkevich isotherm models

4.2.5. Parameters Tabulation

Packing density (g/cm^3)	**0.02**	**0.04**	**0.06**	**0.08**	**0.09**	**0.10**
α_L **(mg/g)**	180	31	15	15.75	15.6	20
k_L **(L/mg)**	10000	1000	333	250	200	250
r^2	0.998	0.997	0.995	0.996	0.997	0.998

TABLE 4.4.: Langmuir isotherm parameters.

Packing density (g/cm^3)	**0.02**	**0.04**	**0.06**	**0.08**	**0.09**	**0.10**
$1/n_F$	0.019	0.033	0.046	0.045	0.040	0.034
k_F **(L/g)**	51.286	29.717	20.324	14.588	11.912	11.776
r^2	0.473	0.549	0.594	0.660	0.671	0.712

TABLE 4.5.: Freundlich isotherm parameters.

Packing density (g/cm^3)	**0.02**	**0.04**	**0.06**	**0.08**	**0.09**	**0.10**
b **(J/mol)**	2473.871	2430.215	2617.549	3716.47	5153.470	6090.465
A **(L/g)**	$1.77x10^{22}$	$4.69x10^{12}$	$2.11x10^{7}$	$3.21x10^{9}$	$5.67x10^{10}$	$3.9x10^{12}$
r^2	0.435	0.544	0.585	0.651	0.662	0.705

TABLE 4.6.: Tempkin isotherm parameters.

Packing density (g/cm^3)	**0.02**	**0.04**	**0.06**	**0.08**	**0.09**	**1.0**
Q_D **(mol/g)**	9162.20	2722.70	1172.20	547.02	337.29	325.09
B_C **(mol^2/kJ^2)**	$-1.0x10^5$	$-2.0x10^5$	$-3.0x10^5$	$-3.0x10^5$	$-3.0x10^5$	$-2.0x10^5$
r^2	0.352	0.457	0.500	0.566	0.578	0.619

TABLE 4.7.: Dubinin-Radushkevich isotherm parameters.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Different model will give different result of which packing density that follow and favourable the adsorption kinetics as well as adsorption isotherms. Using three proposed kinetic models: *Pseudo-first-order, Pseudo-second-order* and *Intra-particle diffusion model*, the elucidation for the practicability and performance of *Ceiba Pentandra* is varies. Pseuo-first-order kinetic shows that the best packing density for practical uses is 0.06 g/cm^3 with the value r^2 of 0.702. For pseudo-second-order, two packing densities are shown the most favourable: 0.90 g/cm^3 and 0.10 g/cm^3 with r^2 of 0.980 and 0.915 respectively with 0.90 g/cm^3 packing density is the best. Furthermore, the intra-particle diffusion models suggest the favourable condition with 0.705 and 0.745, also packing density of 0.90 g/cm^{3}and 0.10 g/cm^3 respectively. Comparing all three kinetic models of adsorption, 0.90 g/cm^3 packing density elucidated by pseudo-second-order suggests the optimum condition for field implementation and mass operation of *Ceiba Pentandra.*

For the adsorption isotherms, four models have been used: *Langmuir, Freundlich, Tempkin* and *Dubinin-Radushkevich* isotherms. Langmuir isotherm shows the best packing densities of 0.02 g/cm^3 and 0.10 g/cm^3 with both elucidate the r^2 value of 0.998. While the rest three isotherms, Freundlich, Tempkin as well as Dubinin-Radushkevich suggest 0.10 g/cm^3 as their favourable packing density with the value of r^2 of 0.712, 0.705 and 0,619 respectively. Comparing all four adsorption isotherms, based from the r^2 performance the Langmuir isotherm with the range value of 0.995-0.998 describe the

adsorption better than the Freundlich isotherm, Tempkin isotherm and Dubinin-Radushkevich isotherm.

However, the result is also prone to flaws. The experimental data is inadequate and also unpredicted for some of the parameter. Due to many factors such as operators, materials, apparatus and surrounding condition, in the future, thorough implementation of careful progress can abating and reducing the unnecessary and any frailty condition.

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APPENDICES

Adsorption kinetics models:

a) Pseudo-first-order

$$\frac{dq}{dt} = k_1(q_e - q)$$

- q_e is the value of adsorbate adsorbed at equilibrium (mg/g)
- q is the amount of adsorbate adsorbed at time t (mg/g)
- k_1 is rate constant for first-order adsorption (min^{-1}).

After integration and the applying of the initial conditions q_t=0 at t=0 and q_t=q_t at t=t, the integrated form of equation becomes:

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303}t$$

- t is adsorbed time (min

b) Pseudo-second-order

$$\frac{dq}{dt} = k_2(q_e - q)^2$$

- k_2 is the rate constant of second-order adsorption (g/mg.min).

After integration is applied into general equation of pseudo-second-order with boundary conditions q_t=0 at t=0, q_t=q_t at t=t, the equation becomes:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$$

The initial sorption rate constant, h (mg/g.min) at t=0 is defined as:

$$h = k_2 q_e^2$$

- k_2 and h values are determined from the slope and intercept of the plots of t/q against t.

c) Intra-particle diffusion model

$$q = K_d t^{1/2} + I$$

- K_d is the intra-particle diffusion rate constant.
- I is the idea about the thickness of the boundary layer.

If intra-particle diffusion occurs, the plotting of q against $t^{1/2}$ will be linear. Intra-particle diffusion also will be the only rate limiting parameter which controlling the process if the line of the plotting pass through the origin [9].

Adsorption isotherm models:

a) Langmuir isotherm

$$\frac{C_e}{q_e} = \frac{\alpha_L C_e}{K_L} + \frac{1}{K_L}$$

- q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (g/g)
- C_e is the equilibrium concentration of the absorbate
- K_L and α_L are the Langmuir adsorption constant (L/mg) and (mg/g) respectively.

b) Freundlich isotherm

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \text{ (logarithmic linear form)}$$

- K_F (L/g) and $1/n_F$ are the Freundlich constants, indicating the sorption capacity and sorption intensity respectively.

The value of $0 < 1/n_F < 1$ indicates that the sorption is favorable [9].

c) Tempkin isotherm

$$q_e = B \ln A + B \ln C_e$$

$$B = \frac{RT}{b}$$

- A is Tempkin isotherm constant (L/g)
- b is a constant related adsorption heat (J/mol)
- R is the gas constant (8.314 J/mol.K)
- T is the absolute temperature (K).

The isotherm constants A and b can determined from intercept and slope from the plot of q_e with ln C_e [9].

d) Dubinin-Radushkevich (D-R) isotherm

$$\ln q_e = \ln Q_D - B_C \varepsilon^2$$

- Q_D is the theoretical maximum capacity (mol/g).
- B_D is the D-R constant (mol^2/kJ^2)
- ε is the Polanyi potential:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e})$$

The constant B related to the mean energy of sorption, E (kJ/mol) which is calculated using the following equation:

$$E = \frac{1}{\sqrt{2B_D}}$$

For adsorption energy, the physical adsorption range has to be in the range of 0.9 – 4 kJ/mol [9].