

**DYNAMIC SIMULATION OF PHENOL ADSORPTION
USING MICROWAVE INDUCED COCONUT SHELL
ACTIVATED CARBON**

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by

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LIST OF SYMBOLS

Symbol	Description	Unit
k_{AB}	Adams-Bohart kinetic constant	L/mg.min
C_b	Bulk concentration of absorbate in solution	mg/L
z	Adsorbent bed height	cm
U_0	Superficial velocity	cm/min
C_0	Initial adsorbate concentration	mg/L
k_{Th}	Thomas model rate constant	mL/min.mg
q_0	Maximum solid phase concentration of the solute	mg/g
V_{eff}	Volume of adsorbate	L
C_t	Adsorbate concentration at time t	mg/L
t	flow time	min
τ	Time required for 50% breakthrough	min
k_{YN}	Yoon-Nelson rate constant	L/min
q_e	Amount of solute removed per unit mass adsorbent	mg/g
w_i	Amount of solute removed per unit mass adsorbent	kmol/kg
q_{max}	Maximum adsorption of the solid phase in monolayer	mg/g
IP_1	Maximum adsorption of the solid phase in monolayer	kmol/kg
k_L	Energy constant related to the heat of adsorption	L/mg
IP_2	Energy constant related to the heat of adsorption	m ³ /kmol
M	Molecular weight of phenol	g/mol
D_m	Molecular diffusion coefficient	m ² /s
D_k	Knudsen diffusion coefficient	m ² /s
D_p	Effective pore diffusivity coefficient	m ² /s
d_p	Adsorbent particle diameter	m
k_{fi}	External film mass transfer coefficient	m/s
K_i	Global mass transfer coefficient	s ⁻¹
R_p	Adsorbent particle radius	m

r_p	Pore radius	m
T	Solution temperature	K
v_i	Interstitial velocity of the solution	m/s
V_m	Solute molar volume at its normal boiling point	cm ³ /mol
V_c	Critical volume	cm ³ /mol
ϵ_p	Particle porosity	dimensionless
ϵ_b	Bed void fraction	dimensionless
τ_p	Tortuosity factor	dimensionless
μ_{sol}	Dynamic viscosity of the solution	kg/m.s
μ_s	Dynamic viscosity of the solvent	kg/m.s
α_A	Association factor of solvent	dimensionless
C_B	Concentration at breakthrough	mg/L
Q	Flow rate	L/min
t_B	Breakthrough time	min
$m_{adsorbent}$	Mass of adsorbent	g
N_o	Saturation constant	mg/L
ϵ^2	Square of normalized error	dimensionless
r^2	Standard measure of goodness of fit	dimensionless
\hat{y}	Estimated values from models	(mg/L)/(mg/L)
y	Experimental data or simulation result	(mg/L)/(mg/L)
\bar{y}	Mean value of experimental data	(mg/L)/(mg/L)
τ_{exp}	Time required for 50% breakthrough from experiment	min
τ_{sim}	Time required for 50% breakthrough from simulation	min

LIST OF ABBREVIATIONS

UNIQUAC	Universal Quasichemical
NRTL	Non-Random Two Liquid
UNIFAC	Universal Functional-Group Activity Coefficients
NRTL-SAC	Non-Random Two Liquid segment activity coefficient
VLE	Vapor-liquid equilibrium
LLE	Liquid-liquid equilibrium
SLE	Solid-liquid equilibrium
Th	Thomas
YN	Yoon-Nelson
AB	Adams-Bohart
IP	Isotherm parameter

PENJERAPAN FENOL MENGGUNAKAN KARBON AKTIF TEMPURUNG KELAPA TERDORONG OLEH GELOMBANG MIKRO

ABSTRAK

Tempurung kelapa merupakan sumber yang murah, mampan dan mudah dapat daripada industri pertanian di Malaysia sebagai bahan mentah untuk menghasilkan karbon aktif dalam proses penjerapan fenol. Dalam kajian ini, simulasi proses penjerapan fenol berterusan dengan menggunakan perisian ASPEN Adsorption akan dijalankan untuk menilai prestasi penjerapan menggunakan karbon aktif tempurung yang terdorong oleh gelombang mikro. Implikasi daripada parameter proses seperti kadar aliran, kepekatan fenol dan ketinggian lapisan karbon aktif dalam proses penjerapan fenol telah dikaji and hasil kajian menunjukkan ketiga-tiga parameter memberikan implikasi yang ketara dalam proses penjerapan. Prestasi penjerapan akan dinilai dengan menggunakan masa bulus dan kapasiti pada masa bulus. Daripada keputusan kedua-dua eksperimen dan simulasi, didapati lebih banyak fenol jerap pada karbon aktif apabila kadar aliran rendah digunakan. Sementara itu, dengan menggunakan kepekatan dan ketinggian lapisan karbon aktif yang lebih tinggi, lebih banyak fenol dijerap oleh karbon aktif. Kelakuan penembusan dalam proses penjerapan fenol telah diramal dengan menggunakan 3 model dinamik iaitu model Thomas, model Yoon-Nelson dan model Adams-Bohart. Ketiga-tiga model dinamik memberikan ramalan yang baik terhadap penjerapan fenol bagi kedua-dua keputusan eksperimen and simulasi kerana nilai r^2 adalah tinggi.

DYNAMIC SIMULATION OF PHENOL ADSORPTION USING MICROWAVE INDUCED COCONUT SHELL ACTIVATED CARBON

ABSTRACT

Coconut shell is a cheap, sustainable, and abundant resources in Malaysia as a raw material for making the activated carbon to be used as adsorbent in the adsorption process. In this study, the adsorption performance of the microwave induced coconut shell activated carbon is tested on the continuous adsorption of phenol by using ASPEN Adsorption software. The effects of the process parameters such as flow rate, initial phenol concentration and adsorbent bed height to the adsorption performance are investigated and the results showed that those 3 parameters have a significant effect on the adsorption performance. The adsorption performance of the phenol by using the microwave induced coconut shell activated carbon is evaluated by using the breakthrough time and the breakthrough adsorption capacity. The phenol adsorption performance is studied for both experiment and simulation and the results show a similar trend on the varying of process parameters. Higher amount of phenol is adsorbed on the activated carbon when the feed flow rate is lowered. In the other hand, the amount of phenol adsorbed also increased as the initial phenol concentration and bed height increased. The breakthrough behaviour of phenol adsorption is predicted by using three dynamic models which are Thomas model, Yoon-Nelson model and Adams-Bohart model. All three models are capable in providing a good fit to both the experimental data and simulation results based on the high r^2 values.

CHAPTER 1 INTRODUCTION

1.1 Research Background

Phenol is widely used in chemical industry which is used as raw material to produce other derivatives such as cresol, aniline, alkylphenols and resins (Careghini *et al.*, 2015). Phenol can be found in petrochemicals, pharmaceutical, pulp, paper and wood products, resin manufacturing, oil refining, plastics and paint, and other industries effluent (Mohammadi *et al.*, 2015). Without effective treatment of these effluents before discharge, human health, animal, and aquatic ecosystem may be jeopardised. US Environmental Protection Agency (EPA) and the National Pollutant Release Inventory (NPRI) of Canada have recognised phenol as a priority pollutant. A strict discharge limits for phenols had been set by international regulatory bodies for a sustainable environment (Sun *et al.*, 2015). For example, the EPA set a water purity standard for phenol in surface water of fewer than 1 ppb (Kazemi *et al.*, 2014). Consumption of drinking water with high phenol concentration will cause gastrointestinal tract problems and muscle tremor with difficulty in walking. Phenol will undergo metabolism once it presents in body system and convert to various reactive intermediates which can form covalent bonds with proteins easily, and toxic effects are exerted on humans (Schweigert, Zehnder and Eggen, 2001). In turn of that, the United States Food and Drug Administration (USFDA) and World Health Organization (WHO) recommended a permitted limit of 0.001 mg/L phenol in drinking water.

The wastewater produced in the industry needs to be treated intensively before discharging to the water bodies. There are several methods in treating wastewater such as photocatalytic degradation, ozonation, extraction, biological method, adsorption, and membrane-based separation method. Compared to other methods, adsorption is an effective, ecologically acceptable, cost effective, and sustainable approach for removing of phenol.

Adsorption is a process in which the adsorbate in the form of ions, atoms, or molecules adhere to the surface of a solid material (adsorbent). The activated carbon is the most extensively employed adsorbent in phenol elimination due to its porous structure with interconnected pores, high adsorption capacity, and favourable ionic nature and surface chemistry (Mohammed *et al.*, 2016). However, the commercial activated carbon is expensive and not cost-effective in large scale operation. Therefore, some natural materials which is low cost and available locally such as bagasse from coconut shell, oil palm waste, wood and etc were used to develop some natural and cheap adsorbents.

In this work, the phenol adsorption by using coconut shell activated carbon will be conducted by using dynamic simulation in Aspen Adsorption® V10 software. Aspen Adsorption® is a comprehensive flowsheet simulator that can be used to design, simulate, optimize, and analyse industrial gas and liquid adsorption processes. Aspen Adsorption® is a powerful tool to design, simulate, troubleshoot, and manage profitable process plant. This enable the plant performance and profitability to be optimized by simulating the adsorption process to determine the optimal process conditions with the adsorbent available. Aspen Adsorption® can be used to simulate solid-liquid adsorption, temperature swing adsorption, and pressure swing adsorption. Aspen adsorption had been used in modelling and simulation for adsorption process like pressure swing adsorption system for hydrogen purification studied by Biswas, Agrawal and Sinha (2010), modelling of adsorption process for post-combustion capture (Plaza *et al.*, 2017), dynamic simulation of melanoidin adsorption from distillery effluent (Ahmed *et al.*, 2020) and etc.

In this work, the phenol adsorption process by using microwave induced coconut shell activated carbon will be simulated by using Aspen Adsorption® V10. The performance of the packed bed adsorption of phenol will be studied. The outcome of this paper can then be applied in the effluent treatment from phenol derivatives manufacturing factories.

1.2 Sustainability of Phenol Adsorption using Coconut Shell Activated Carbon

Phenol is a phenolic compound that presents in the industrial effluent from various industry such as manufacturing of plastics and resins, agrochemical, pharmaceutical, and etc. Phenol also can be found in domestic water at low concentration as it widely presents in the household items. Therefore, the industry effluent and domestic wastewater which contain phenol which is a hazardous chemical needs to be treated before release to water bodies.

Adsorption is a tertiary wastewater treatment which is a final cleaning process that the wastewater quality can be improved before it is reused, recycled or discharge to the environment. In this project, microwave induced coconut shell activated carbon is used as adsorbent in adsorbing the phenol in the water. The sustainability of phenol adsorption utilising activated carbon from coconut shell is being studied.

The sustainability of phenol adsorption utilising activated carbon from coconut shell will be studied from the perspective of Sustainable Development Goals (SDGs). The cleanliness and hygiene of water is related to SDG 6: Clean Water and Sanitation and SDG 14 Life below Water. In SDG 6: Clean Water and Sanitation, the wastewater from the industry is properly collected, treated, and discharged to remove the pollutants in this case will be phenol to improve sanitation. The wastewater from the industry which contains phenol can be treated by using adsorption to certain standards and it can be reused, recycled in the industry, or being discharged to the environment. The wastewater which contains phenol can be treated using activated carbon adsorption before it is released to water bodies as the water sources from water bodies will be the water supply for downstream communities.

In the other hand, for SDG 14: Life below Water, the wastewater which contains phenol which is a hazardous chemical will affect the growth of the aquatic organisms will be treated using adsorption before releasing to water bodies. There is also a proposed SDG on water, with sub-goals for the enhancement of water quality through wastewater management, which aims

to manage water for the long-term sustainability of people and the environment (Malik *et al.*, 2015). For the improvement in water quality and wastewater management, there are few targets by 2030: 1) Reduce both the urban population with untreated industrial wastewater flows by [X%]; 2) Increase urban and industrial wastewater reused safely by [Y%] and 3) Reduce nutrient pollution from agriculture by [Z%]. Therefore, these Sustainable Development Goals (SDGs) and its sub-goals can be achieved in the future by proper treatment of wastewater and activated carbon adsorption can be used as one of the treatments.

Other than that, the adsorbent used is also derived from a renewable agricultural waste which is coconut shell. Coconut shell has many usage other than being processed as activated carbon and coconut shell charcoal is one of the domestic and industrial fuels that is used to produce heat energy. Powder of coconut shell is also being used substantially in the manufacturing of mosquito coils and incense sticks. Coconut shell can also be used in manufacturing of resin glue as filler and as a phenolic extruder in plywood manufacturing. It has uniform quality and good water and fungal attacks resistance.

Coconut shell is an agricultural by-products which is a promising feedstocks for sustainable activated carbon production. Coconut shell is an ideal raw material for activated carbon production since there are many coconut plantations in Malaysia, which can increase the manufacturing process' economic feasibility and its high density and purity properties (Arena, Lee and Clift, 2016). The use of coconut shell as raw material for activated carbon manufacturing can minimize the greenhouse gases emissions when coconut shells rot or are incinerated. Hence, the phenol adsorption process using microwave induced coconut shell activated carbon is a sustainable process from the perspective of Sustainable Development Goals (SDGs) and the raw material of adsorbent which is a renewable source from the agricultural waste.

1.3 Problem statement

In the past, researchers had investigated the removal of phenol by adsorption using activated carbon. In fixed-bed phenol adsorption studies by Garba *et al.* (2016), the maximum adsorption capacity of the modified palm shell-based activated carbon for phenol was 238.12 mg/g at breakthrough time at 250 mg/L initial phenol concentration, 1cm bed depth, and 9 mL/min flow rate. The palm shell-based activated carbon was made using a two-step activation technique. First, the oil palm shell was carbonized at 800 °C for 2 hours then impregnated with potassium carbonate solution, K₂CO₃ at a ratio of 2 g of activant to 1 g of char.

There were also researchers that studied the performance of adsorption in packed bed column by using dynamic simulation in Aspen Adsorption®. Ahmed *et al.* (2020) studied the melanoidin adsorption from distillery effluent using fly ash adsorbent and Juela (2020) studied the adsorption of acetaminophen using sugarcane bagasse and corn cob activated carbon as adsorbent by dynamic simulation in Aspen Adsorption®.

For phenol adsorption, Anisuzzaman *et al.* (2016) studied the performance of phenol adsorption in packed bed column packed with dates' stone activated carbon by dynamic simulation in Aspen Adsorption® V7.1 software. On phenol adsorption, the impacts of process parameters such as column length, inlet flow rate, and initial phenol concentration were examined. Anisuzzaman *et al.* (2016) proposed a small-scale adsorption column as an ideal drinking water treating system that is suitable for a single household.

However, Aspen Adsorption® simulator still not widely use in the study of adsorption of phenol by using fixed bed column. Experiments need to be carried out to investigate the influence of process parameters on phenol adsorption. This is time consuming and there are some process parameters that difficult to control such as the operating temperature of adsorption. By using Aspen Adsorption® simulator, the operating conditions such as flow rate, temperature, pressure, initial concentration can be specified, and the performance of fixed bed

adsorption can be simulated and predicted. By using Aspen Adsorption®, the cost of adsorbent development and optimal process conditions determination can be reduced. Hence, in this paper, phenol adsorption simulation will be carried out by using Aspen Adsorption® and error analysis will be done to compare between the experimental data and the simulation result.

1.4 Objective

The aims of this article are as described as below:

1. To investigate the effect of concentration of adsorbate, the flow rate of adsorbate and the bed height on the adsorption of phenol using ASPEN Adsorption simulation.
2. To compute the adsorption capacity of breakthrough of phenol.
3. To analyse the fixed bed adsorption data with the dynamic model.

CHAPTER 2 LITERATURE REVIEW

2.1 Batch and Column Adsorption

There are two adsorption modes which are batch adsorption and column adsorption. The adsorbent is submerged in the solution during batch adsorption, and the solution maintains in contact with the adsorbent. The adsorption process ongoing and ceases when equilibrium condition between the adsorbate and the adsorbent is established. In the other hand, the feed solution continuously flows inside the packed bed and in contact with the adsorbent in the continuous adsorption process with the employing of packed column. The adsorption process will be stopped when the adsorbent is saturated with the adsorbate on its active site in which the concentration of the adsorbate exiting the adsorbent is 90-95 % of the initial concentration (Girish and Murty, 2016).

Previous adsorption research was limited to batch adsorption studies due to the huge amount of adsorbent material needed is unavailable (Vijayaraghavan *et al.*, 2004). In the industrial scale, batch adsorption technique may not be suited for handling the high flow rate wastewater that needs to be treated (Karunaratne and Amarasinghe, 2013). However, the batch adsorption is utilised in such experiments to determine the process and adsorbent effectiveness in removing certain adsorbates, as well as the maximum adsorption capacity (Ahmad and Hameed, 2010). In batch adsorption process, the same solution remains in the system after the equilibrium is established. Therefore, the adsorbent may not be effectively utilized, and this causes the decreasing of adsorption efficiency. As a result of this, both the volume of treated effluent and the adsorption capacity are reduced. (Dwivedi *et al.*, 2008).

Continuous adsorption is introduced to overcome all those difficulties faced in batch adsorption. As the feed solution is continuously in touch with the adsorbent, the adsorbate will eventually occupy all of the active sites on the adsorbent, and the adsorbent will be fully

depleted. As a result, there are various benefits to adopting packed bed column adsorption, including simple operation, handling of high influent flow rates, increased yield, and process scale-up (VAZQUEZ *et al.*, 2006). The concentration difference acts as the driving force for the adsorption process to occur in the packed column adsorption process, resulting in a higher adsorption efficiency and a higher quality effluent (Aksu and Gönen, 2004). Aside from that, the packed column adsorption process can be used to treat wastewater containing various contaminants discharged by various industries (Tepe and Dursun, 2008). Larger volume of wastewater released from the industry can also be treated as compared with the batch adsorption process.

Based on the comparison between the batch and the continuous adsorption, a clear deduction can be made that the batch adsorption is not feasible for treating wastewater in an industrial scale. This is due to a long period of time is required per batch to reach the equilibrium and low wastewater treatment capacity, even though the adsorption capacity is higher. Thus, in this research, the fixed bed column adsorption will be focussed on instead of batch adsorption.

2.2 Type of Adsorbent

In an adsorption process, adsorbent plays an important role in an efficient adsorption process. Therefore, an adsorbent with higher adsorption capacity and cost-effective need to be chosen to improve the removal efficiency of the adsorbate at lower cost. There are several types of adsorbent that can be used to remove the phenol that present in wastewater such as activated carbon, synthetic resin, and zeolite, etc. Activated carbon is the most often utilised adsorbent for removing a variety of organics from wastewater. However, the commercial activated carbon has higher cost, and it is not suitable to be used in industrial scale. Recently, some cheap and natural adsorbents have been developed. Some low-cost adsorbents can be produced from some

natural materials which are low-cost and available locally such as clay, red mud, bagasse, zeolites, or some waste by-products from industrial operations such as coal, fly ash, and industry wastes. Table 2-1 shows the alternative feed stocks that can be used to prepare the activated carbon and low-cost adsorbent used in treating of wastewater.

Table 2-1 Proposed alternative feed stocks that can be used in preparing low-cost adsorbents and activated carbon that used in treating of wastewater (Pollard *et al.*, 1992; Mohan and Singh, 2005).

Alternative feed stocks		
Bones	Fertilizer waste slurry	Petroleum acid sludge
Bagasse	Fish	Pulp-mill waste
Bark	Fruit pits	Palm tree cobs
Beat-sugar sludge	Graphite	Petroleum coke
Blood	Jute stick	Petroleum acid sludge
Blue dust	Kelp and seaweed	Potassium ferrocynide residue
Carbohydrates	Lignin	Rubber waste
Cereals	Lignite	Rice hulls
Coal	Lampblack	Refinery waste
Coffee beans	Leather waste	Reffination earth
Coconut shell	Municipal waste	Scrap tires
Coconut coir	Molasses	Sunflower seeds
Cottonseed hulls	Nut shells	Spent Fuller's earth
Corncobs	News paper	Tea leaves
Distillery waste	Oil shale	Wheat straw
Fuller's earth	Olive stones	Wood

As shown in Table 2-1, most of the alternative feed stocks are biomass that mainly derived agricultural solid waste or food industry waste which are preferable options for activated carbon precursors.

These biomass resources are abundant, renewable, and cheaper to be used in producing activated carbon. Coconut is Malaysia's fourth most significant industrial crop, after oil palm, rubber, and paddy. The total coconut production in Malaysia was 504,722 tonnes/year with an average yield of 5.97 tonnes/hectare.year in 2016 (kek hoe, 2018). As a result, a huge amount of agricultural waste is generated each year in the form of fibre and shell. Following harvest,

the trash is either left to rot in the coconut plantation or used as a burning fuel, both of which contribute to pollution. Thus, the transformation of coconut shell solid waste into activated carbon is one of the practical way to manage the huge amount of waste and produce a cost-effective adsorbent.

Coconut shell has a similar chemical composition with hard wood which consists of lignin and cellulose as the major components (Rodrigues and Pinto, 2007). Coconut shell is an excellent raw material for converting into activated carbon because of its hardness and abrasion resistance. This reduces the creation of carbon fines during the adsorption process. With this, there is no additional separation step is needed to separate the carbon fines from the treated water.

In conclusion, coconut shell is a suitable raw material that can be used in the production of adsorbent which is cost effective. Besides, coconut shell-based activated carbon has the higher hardness and higher abrasion resistance which makes it an ideal choice for water purification compared to other types of activated carbon that are made by using different materials.

2.3 Adsorption Mechanism of Phenol

The adsorption mechanism of phenol on the adsorbent need to be studied to improve the adsorption performance. There are three mechanisms that have been proposed which are $\pi - \pi$ dispersion interaction mechanism, the hydrogen bonding formation mechanism and the electron donor-acceptor complex mechanism (Moreno-Castilla, 2004). For $\pi - \pi$ dispersion interaction mechanism, Coughlin and Ezra (1968) suggested that dispersive forces between the π -electrons in the phenol and the π -electrons in the activated carbon are involved in the phenol adsorption on the activated carbon.

Next is the hydrogen bonding formation mechanism. Hydrogen bond is a dipole-dipole interaction between the hydrogen atom and the high electronegative atom. There are two criteria for the formation of hydrogen bonding: 1) the hydrogen atom in a molecule must bond with a strongly electronegative atom such as fluorine, chlorine, and oxygen; 2) the hydrogen atom must be in a vicinity of another strongly electronegative atom with lone pair electron. The adsorbate, phenol can form hydrogen bond with the functional groups on the adsorbent surface such as hydroxyl group, carbonyl group, etc.

The last mechanism is the electron donor-acceptor complex mechanism. The aromatic compound, phenol adsorbs on the adsorbent by a donor-acceptor complex mechanism in which the carbonyl oxygen on the surface of the activated carbon works as an electron donor and the aromatic ring of phenol functions as an acceptor (Mattson *et al.*, 1969). Once the carbonyl groups are exhausted, the aromatic molecule, phenol forms a donor-acceptor complex with the rings of the basal plane. After carbon oxidation, the carbonyl group oxidise to create carboxyl groups, resulting in a decrease in phenol adsorption. As a result, the electron donor-acceptor complexes cannot be form and the adsorption capacity will decrease.

2.4 Effect of Parameters on the Adsorption Capacity

2.4.1 Effect of Initial Concentration

One of the factors that will affect the efficiency of the adsorption is initial phenol concentration. The mechanism of the adsorption consists of three consecutive steps in transfer of solutes in liquid onto the adsorbents (Khamidun and Abdul Rahman, 2017). The first step is external mass transfer, which transports the adsorbate from the bulk solution to the grain's external film zone, which connects the pores immediately. The second step is the internal mass transfer in which the adsorbate diffuses from the film zone towards the adsorbent's acceptor sites. The last step is fixation in which the adsorbate attaches onto the acceptor sites on the

interior of the adsorbent grain. The rate-limiting steps in adsorption are external mass transfer and intra-particle diffusion (Nassar *et al.*, 2008). Dilute solute concentration usually is one of the causes of the external mass transfer as the rate-limiting step (Girish and Murty, 2016). The initial concentration of the solute, which is the driving force in solute diffusion, affects the rate of mass transfer of the solute. According to Fick's diffusion law states, the diffusive flux from a high-concentration region to a low-concentration region is proportional to the concentration gradient. Therefore, the rate of mass transfer in adsorption is directly proportional to the concentration gradient of the solute. The effect of phenol initial concentration on the adsorption efficiency is shown in Table 2-2.

Table 2-2 Performance of phenol adsorption in different initial phenol concentration.

Adsorbent	Total surface area (B.E.T.) (m ² g ⁻¹)	Flow rate (mL/min)	Bed Height (cm)	Phenol initial concentration (mg/L)	Exhaustion time (min)	Removal efficiency (%)	Article
Walnut shell activated carbon (WSA)	1000	40	4	20	1020	98.1	(Ahma dineja d <i>et al.</i> , 2020)
				60	420	55.7	
				100	240	25.2	
Coconut shell activated carbon (CSA)	1150	6	3	20	1025	74.2	(Garba <i>et al.</i> , 2016)
				60	540	59.6	
				100	300	2.4	
Potassium carbonate synthesized activated carbon (PCAC)	707.8	6	3	50	660	-	(Garba <i>et al.</i> , 2016)
				250	360	-	

As shown in Table 2-2, when the phenol initial concentration increased, the exhaustion time of the adsorption bed decreased, and the removal efficiency also decreased. The driving force, which is the concentration gradient, increases as the phenol initial concentration rises, enhancing the rate of phenol diffusion within the adsorbent particles. The binding sites of the adsorbent saturated faster and the column becomes saturated at a shorter period. The exhaustion time and the removal efficiency both dropped when the initial phenol concentration was

increased. Therefore, to improve the removal efficiency and achieve longer exhaustion time, the influent phenol concentration must be reduced.

To determine the range of initial phenol concentration to be tested in the experiment, the phenol concentration in the wastewater from industries is reviewed. The phenol concentration in wastewater discharged by various industries is shown in Table 2-3. There is a wide range of the phenol concentration which is 1.1 – 7000 mg/L. In this simulation for initial phenol concentration, the concentration tested will be scaled down where the tested range would be 10 – 50 ppm (9.9565 – 49.7825 mg/L) to be compared with the results from the experiment.

Table 2-3 Phenol concentration in wastewater from various industries (Girish and Murty, 2016).

Industrial source	Phenol concentration, mg/L
Petroleum refineries	40–185
Petrochemical	200–1220
Textile	100–150
Leather	4.4–5.5
Coke ovens	600–3900
Coal conversion	1700–7000
Ferrous industry	5.6–9.1
Rubber industry	3–10
Pulp and paper industry	22
Wood preserving industry	50–953
Phenolic resin production	1600
Phenolic resin	1270–1345
Fiberglass manufacturing	40–2564
Paint manufacturing	1.1

2.4.2 Effect of Flow Rate

Flow rate of the solution is another factor that will affect the efficiency of the phenol adsorption in which flow rate will affect the contact time of the adsorbate with the adsorbent. The residence time of the solution in the column will be longer when the flow rate is lower, the adsorbate will have a longer time to interact with the adsorbent until equilibrium is achieved. To extend solution residence time in the column and achieve better adsorption capacity, the flow rate of the solution must be reduced. A plateau in the bed adsorption capacity will be achieved where there is no change in the bed capacity even when the flow rate is continued to

be reduced although the adsorption process can be operated in a very slow manner (Crini and Badot, 2010). This is due to the adsorbate must be able to overcome the mass transfer resistance for the adsorption process to occur. A minimum flow rate is needed to provide a sufficient axial transport for the adsorbate to engage in intra-particle diffusion. Moreover, it is not practical to operate the adsorption process at a very low flow rate as a column with a large volume is needed to retain the wastewater effluent in the column due to long residence time is required. Therefore, an optimum flow rate needs to be determined to achieve a maximum bed capacity with a fixed amount of adsorbent.

Whereas, with the increasing of flow rate, the boundary layer at the adsorbent surface will become thinner as the inertia of the fluid will be much significant compared to the viscous force (Crini and Badot, 2010). A turbulence flow is also being induced when the flow rate increased. The mass transfer resistance will be reduced due to the thinner boundary later and turbulent flow which will improve the adsorption rate. However, the flow rate cannot be increased beyond the limiting flow rate as it will have a negative impact to the adsorption rate. This is because prior to the diffusional mass transfer to happen, the adsorbate must be in contact with the adsorbent for a certain amount of time. If the flow rate is too high, the contact time between the adsorbate with the adsorbent will not be long enough for the adsorption to occur. Short circuiting might also occur when the flow rate is increased (Crini and Badot, 2010). Short circuiting in the adsorption column is a phenomenon whereby the adsorbent is not fully wetted since the fluid tends to flow through a preferred path due to inertia force. The fast-moving fluid mostly will travel straight instead of diverging to the side of the column, and this causes the adsorbent will not be fully utilized. This will lead to the misconception that the adsorption column has a shorter breakthrough time and exhaustion time.

The effect of flow rate on the adsorption performance was studied by the researchers and is shown in Table 2-4. As shown in Table 2-4, as the flow rate increases, the adsorption

bed's exhaustion period decreases, and the breakthrough curve steepens. The residence time of the adsorbate in the column reduced as the flow rate increased, causing the solution to exit the column before the system reached equilibrium. Hence, the adsorption capacity decreased and affect the adsorption performance. Therefore, the flow rate of the solution needs to be adjusted so that an optimum condition can be maintained to obtain a maximum adsorption capacity and with a longer bed service time. When the process is mainly internal diffusion dependent, the adsorption capacity is usually higher at a lower flow rate.

Table 2-4 Performance of phenol adsorption in different flow rate.

Adsorbent	Total surface area (B.E.T.) (m ² g ⁻¹)	Phenol initial concentration (mg/L)	Bed height (cm)	Flow rate (mL/min)	Exhaustion time (min)	Reference
pulp and paper mill-based activated carbon	907.2	140	2	2	95	(Masomi <i>et al.</i> , 2015)
				3.5	75	
				5	35	
Commercial Activated Carbon	-	100	6	2	432	(Ekpete, Jnr and Horsfall Jnr, 2011)
				3	270	
				4	114	
Corn cob activated carbon	-	500	5	18.3	280	(D. Rocha, S. Franca and S. Oliveira, 2015)
				25.6	210	
				33	180	

2.4.3 Effect of Bed Height

Another process parameter that affects adsorption capacity is the adsorbent bed height in the adsorption column. The adsorbent bed height is higher when the adsorbent dosage is higher. Table 2-5 shows the influence of adsorbent bed height on phenol adsorption. As shown in Table 2-5, both the saturation time of the adsorption column and the phenol removal efficiency increase as the bed height increases. This is owing to the fact that the increased of active sites on the adsorbent surface in the column as the increasing of adsorbent. As a result, more phenol molecules are adsorbed on adsorbent surfaces, broadening the mass transfer zone.

In other words, increasing the bed height increases the adsorption capacity, allowing for the processing of a larger volume of effluent solution.

In the other hand, the saturation time and phenol removal efficiency decrease when the bed height decreases. This is because of the limited number of active binding sites on the adsorbent and the lack of time for the adsorbate to diffuse into the adsorbent's inner pores, saturation of the adsorbent occurs faster (Taty-Costodes *et al.*, 2005).

Table 2-5 Performance of phenol adsorption with different bed height.

Adsorbent	Total surface area (B.E.T.) (m ² g ⁻¹)	Flow rate (mL/min)	Phenol initial concentration (mg/L)	Bed height (cm)	Saturation time (min)	Phenol removal efficiency (%)	Reference
Walnut shell activated carbon (WSA)	1000	40	100	4	300	-	(Ahmadinejad <i>et al.</i> , 2020)
Coconut shell activated carbon (CSA)	1150			8	600	-	
Potassium carbonate synthesized activated carbon (PCAC)	707.8	6	50	4	240	-	
Commercial activated carbon	-			8	420	-	
				1	120	-	(Garba <i>et al.</i> , 2016)
				2	300	-	
				3	540	-	
		2	100	3	282	79.59	(Ekpete, Jnr and Horsfall Jnr, 2011)
				6	570	84.53	
				9	840	85.56	

2.5 Thermodynamics Models to Predict the Phase Equilibria

The adsorption also influenced by the nature of the adsorbate. In general, the extent of a solute's adsorption on the adsorbent and its solubility in the solvent in which it occurs are expected to have an inverse relationship (Jørgensen, 1979). This is the so-called Lundilius' rule, which may be used to anticipate the effect of a solute's chemical character on its uptake from solution (water) in a semi-quantitative manner. Therefore, a suitable thermodynamics

model needs to be selected in the Aspen Adsorption simulation in order to predict the equilibrium and the solubility of solute in the solution.

In the Aspen Adsorption simulation, it is important to anticipate the equilibrium of the components in the system. There are several thermodynamics models that are commonly used in the prediction of the equilibrium of mixture which are Wilson, UNIQUAC, NRTL, Hansen, UNIFAC and NRTL-SAC.

Wilson's model was one of the first thermodynamics model for predicting a non-ideal equilibrium. For binary and miscible systems, it is based on molecular considerations. The model comprises two variables, A_{12} and A_{21} , which relates them to the molar volumes of pure component and interaction energies of binary system derived from experimental data. Wilson's approach, though being one of the first to be used, has some flaws. First, Wilson's model equations are ineffectual for systems in which the activity coefficients logarithms reach maximum or minimum values. Another drawback of Wilson's model is that it is solely good for forecasting the solubilities in totally miscible liquid systems or in confined regions where only one liquid phase exists (Rowlinson, 1970).

Other models were developed as a result of the need to measure the solubilities of pharmaceutical products and polymers in order to overcome some of Wilson's model shortcomings. The solubility parameters in the Hansen model were obtained by doing mathematical regression of the experimental solubility data (Srinivas *et al.*, 2009). The Hansen model was developed using solubility parameters, and it has shown to be a useful tool in the industrial applications, assisting in solvent selection and serving as a corrective model (Hansen, 2007).

Other than the Hansen model, the UNIFAC model, which is developed based on the concept of functional group, is the most successful way for predicting LLE, VLE and SLE (Nouar *et al.*, 2016). Using chemical structural information of the molecules that exist in the

system and some binary interaction coefficients, the model estimates components' activity coefficients that present in the mixture and the system equilibrium (Chen and Song, 2004; Nouar *et al.*, 2016).

Although both the UNIFAC and Hansen models are applicable to a wide range of systems, they do have significant restrictions. For instance, the models are poor to predict the solubility of either large molecular weight molecules or systems comprising electrolyte solutes (Chen and Song, 2004). In addition, Hansen's model is based on a basic assumption that links the solubility parameters to the experimental results; nonetheless, the method has limited relevance in terms of drug solubility (Mota, 2010). As there are parameters for binary interactions and specific functional groups are not known in some circumstances, the UNIFAC method may not be suitable for predicting the system's equilibrium (Adjiman *et al.*, 2010; Valavi *et al.*, 2016). Therefore, there are other models had been developed.

Non-Random Two-Liquid (NRTL) model was derived by Prausnitz *et al.* (1999) which is similarly to the Wilson's model that also considered the local composition concept. The NRTL model is one of the most widely used thermodynamic models in the chemical industry for presenting nonideal VLE and LLE systems with precision (Chen and Song, 2004). The NRTL model predicts the solubility of partially immiscible phases in an extremely nonideal systems more accurately (Rowlinson, 1970).

There is also another thermodynamics models which is NRTL-SAC. The liquid non-idealities are defined by the NRTL-SAC model in terms of three distinct conceptual molecule segments: hydrophilic, polar, and hydrophobic. Chen and Song (2004) developed the NRTL-SAC model as a unique variant method for describing liquid-liquid equilibrium systems, considering the successful area of NRTL industrial applications, particularly in the polymer industry, as well as the constraints of group contribution models. The NRTL-SAC model

requires less experimental work to estimate the solute's solubility in various solvents (Fakhraian *et al.*, 2016).

In conclusion, either the NRTL or NRTL-SAC thermodynamics models can be used in the Aspen Adsorption simulation to predict the solubility of the adsorbate, phenol, and the equilibrium of the system more accurately.

2.6 Dynamic Model

Mathematical models are developed to describe the breakthrough curve in an adsorption process without constantly carrying out the experiment. Preliminary experiments are carried out to determine the constant values that are needed in the model such as rate constant, kinetic coefficient, adsorption capacity, etc. Thus, nonlinear curve fitting is done on the simulation data obtained to determine the most suitable mathematical model to anticipate the dynamic behaviour of phenol adsorption by using activated carbon. The mathematical models that are proposed to predict the dynamic behaviour for the simulation are Adams-Bohart model, Yoon and Nelson model and Thomas model.

The first model is Adams-Bohart model, which was proposed by Bohart and Adams in 1920 while researching the typical chlorine-charcoal transmission curve. The uptake rate of chlorine is proportional to the concentration of the chlorine presents in the bulk fluid and the remaining adsorptive capacity of charcoal yield two equations, as shown below.

$$\frac{dq}{dt} = -k_{AB}qC_b$$
$$\frac{dC_b}{dz} = -\frac{k_{AB}}{U_0}qC_b$$

where k_{AB} (L/mg.min) is the Adam-Bohart model's constant, C_b (mg/L) is the adsorbate concentration in bulk solution, z (cm) is the bed height, U_0 (cm/min) is the superficial velocity. A few conditions are identified to solve the differential equations (Bohart and Adams, 1920):

1) The concentration field is low such that the effluent concentration, C will not exceed 0.15 times of the initial concentration; 2) When time is at infinity, q equals to N_0 when N_0 is the maximum adsorption capacity; 3) At time equals to zero. the residual adsorptive capacity is equal to the maximum adsorptive capacity; 4) When z is equal to zero, the concentration of the adsorbate is the same as the initial concentration. There are also few of assumptions are made in which the bed is homogenous, and the gradients happen only in axial direction. The solved equation is shown as below (Song *et al.*, 2015):

$$\ln\left(\frac{C}{C_0}\right) = k_{AB}C_0t - k_{AB}N_0\left(\frac{z}{U_0}\right)$$

The second model, Thomas model, which assumes second-order reversible kinetics and the Langmuir isotherm, is often used to predict the adsorbent's adsorption capacity and the breakthrough curve (Han *et al.*, 2008; Ghasemi *et al.*, 2011). The second order rate equation for adsorption is expressed as below:

$$\frac{d\theta_t}{dt} \approx k_1(\theta_e - \theta_t)^2$$

where k_1 is a constant, θ_t is the proportion of the surface taken by adsorbate, θ_e is when θ_t had reached equilibrium where $d\theta_t/dt$ is equal to zero. The constant k_1 is composed of initial concentration, C_0 , maximum adsorption uptake, q_{max} , the amount of adsorbent, X as well as the rate constant for adsorption and desorption. The equation that relates them all is as shown as below:

$$k_1 = \sqrt{k_a^2(C_0 - q_{max}X)^2 + 2k_a k_d(C_0 + q_{max}X) + k_d^2}$$

From these assumptions as the base for deriving the Thomas model's expression, the expression is obtained (Sarici-Özdemir, 2014):

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{Th}}{Q}(q_0 m_{adsorbent} - C_0 V_{eff})\right)}$$

where k_{Th} (mL/min.mg) is the Thomas model's rate constant, q_0 (mg/g) is the maximum solid phase concentration of the solute and V_{eff} (L) is the volume of adsorbate. When the exterior and internal diffusion resistances are low, the Thomas model is the best fit to represent the dynamic behaviour of adsorption.

Last but not least, the Yoon-Nelson model is also one of dynamics model that can be used to anticipate the operation period of an adsorption column before it needs to be regenerated. This model is extremely concise in form which supposing that the decrease in the probability of each adsorbate to be adsorbed is proportional to the probability of its adsorption and the breakthrough on the adsorbent (Yoon and Nelson, 1984). The linear form of Yoon-Nelson model is given as below (Rouf and Nagapadma, 2015):

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - \tau k_{YN}$$

Where, C_0 (mg/L) is the initial phenol concentration, C_t (mg/L) is phenol concentration at time t , t (min) is flow time, τ (min) is time taken for 50% breakthrough and k_{YN} (L/min) is Yoon-Nelson rate constant. The Yoon-Nelson model is a simpler models in that it does not need specific information on adsorbate and adsorbent's properties, as well as the characteristics of the fixed bed. Besides that, due to its rough structure, the Yoon-Nelson model is less valuable or convenient for obtaining process variables and predicting adsorption under a variety of situations (Xu, Cai and Pan, 2013).

CHAPTER 3 METHODOLOGY

3.1 List of Materials and Apparatus

The simulation of the phenol adsorption by using microwave induced coconut shell activated carbon in packed bed column was carried out by using ASPEN Adsorption® V10. The adsorbent's physical properties were obtained from the study by Mohd Din et. al. (2009).

3.2 Flow Chart

A flow chart depicting the timeline of the current research endeavour is presented below:

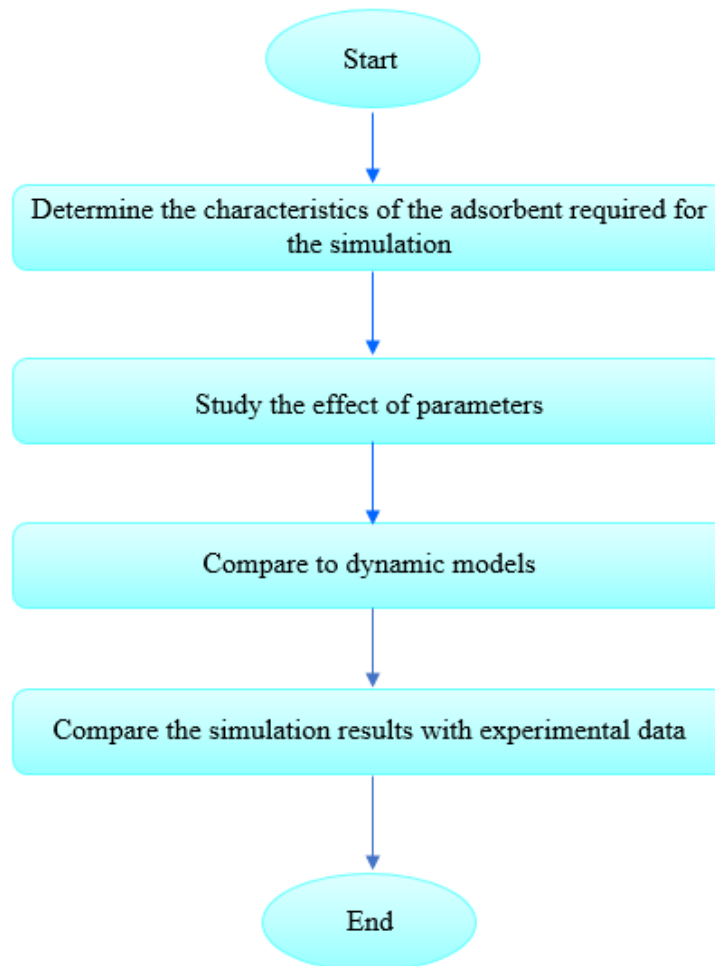


Figure 3.1 Flow chart for the chronology of the current research project.

3.3 Determination of Isotherm Parameters (IP) Values in Simulation

For the phenol adsorption on coconut shell activated carbon, the Langmuir isotherm was employed as the suitable equilibrium model in this study (Mohd Din, Hameed and Ahmad, 2009). Langmuir isotherm is expressed in equation as shown in below:

$$q_e = \frac{q_{max} \cdot k_L \cdot C}{1 + k_L C} \quad w_i = \frac{IP_1 \cdot IP_2 \cdot C}{1 + IP_2 \cdot C}$$

The equation on the left is the generic form of the Langmuir isotherm, whereas the equation on the right represents isotherm presentation in the ASPEN Adsorption®.

The values of IP_1 and IP_2 were determined by using the equation as shown in below:

$$IP_1 = \frac{q_{max}}{1000M}; \quad IP_2 = 1000k_L M$$

3.4 Determination of Global Mass Transfer Coefficient

To set up the Aspen Adsorption simulation, the global mass transfer coefficient was determined. The global mass transfer coefficient (K_i) and its corresponding resistance are presented in Eq. (1) (Tavan *et al.*, 2019).

$$\frac{1}{K_i} = \frac{R_p}{3k_{fi}} + \frac{R_p^2}{15\varepsilon_p D_p} \quad (1)$$

Where, the effective pore diffusivity coefficient (D_p) was estimated using the following correlation (Tavan *et al.*, 2019).

$$\frac{1}{D_p} = \tau_p \left(\frac{1}{D_m} + \frac{1}{D_k} \right) \quad (2)$$

The molecular diffusion coefficient (D_m) was estimated using the following equations for nonelectrolytes in an infinitely dilute solution (Wilke and Chang, 1955).

$$D_m = 7.4 * 10^{-8} \frac{(\alpha_A M_s)^{0.5} T}{\eta_s V_m^{0.6}} \quad (3)$$

In Eq. (3), D_m is in $\text{cm}^2 \text{s}^{-1}$, M_s is solvent molecular weight (g/mol), T is temperature (K), μ_s is the dynamic viscosity of solvent (kg/m.s), α_A is the association factor of solvent, and V_m is solute molar volume at its normal boiling point (cm^3/mol). For phenol, V_m might be estimated from Eq. (4) obtained from Wilke and Chang (1955).

$$V_m = 0.285 V_c^{1.048} \quad (4)$$

The Knudsen diffusion coefficient (D_k), and the tortuosity factor (τ_p) were estimated by Eqs. (5), and (6), respectively (Tavan *et al.*, 2019).

$$D_k = 97 r_p \left(\frac{T}{M_s} \right)^{0.5} \quad (5)$$

$$\tau_p = \varepsilon_p + 1.5(1 - \varepsilon_p) \quad (6)$$

The external film mass transfer coefficient (k_{fi}) was calculated using Eq. (8) (OHASHI *et al.*, 1981).

$$Sh = \frac{k_{fi} d_p}{D_m} = 2 + 1.58 Re^{0.4} Sc^{1/3} \quad (7)$$

Where Reynolds number and Schmidt number were estimated by Eq. (8).

$$Re = \frac{d_p v_s \rho_{sol}}{\mu_{sol}}; \quad Sc = \frac{\mu_{sol}}{\rho_{sol} D_m}; \quad (8)$$