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Removal of Phenol from Wastewater Using Activated Carbon-Based Column: Simulation and Experimental Study

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Abstract

Wastewater treatment has become a community necessity due to the lack of available water resources. As the wastewater contains some pollutants such as phenol, which is known to be highly toxic and corrosive, it must be treated using an effective process. Adsorption is one of the most used methods to get rid of several water pollutants and showing effective results. This study focuses on the feasibility of using aspen adsorption program (ADSIM) to simulate literature experimental work on the phenol adsorption process using activated carbon packed-bed column, and how much is the results are harmonized with each other's. It was looking up for a scientific paper that was performed the adsorption process experimentally and containing the required data to start the simulation by ADSIM, then these data were applied in ADSIM. After that, a comparison study between the obtained results from the literature and ADSIM were done. Several factors were governed including breakthrough time and removal efficiency. Mass transfer coefficient (MTC) was estimated by the ADSIM. For initial concentration 150 mg/L, MTC was 0.605 min^{-1}. At flow rate equal to 10 mL/min, MTC was 0.684 min^{-1} while at bed height equal 5 cm, MTC was 0.505 min^{-1} . Moreover, the effect of initial phenol concentration (100, 150 and 250 mg /l), feed flow rate (10, 15 and 20 ml/min) and bed height (5,10 and 15 cm) were studied. ADSIM results showed that the highest removal efficiency after 2 hr was achieved at 10 mL/min flow rate (%R = 67.6), 10 cm bed height (%R = 45.1) and 150 mg/L initial phenol concentration (%R = 45). The breakthrough time decreases as the flow rate increases (at Q=15 mL/min, the breakthrough time was 24 min while at Q = 20 mL/min, the breakthrough time was 16 min). Also, as the initial concentration increases the breakthrough time decreased (at C_0 = 100 mg/L, breakthrough time was 24 min while at C_0 = 250 mg/L, breakthrough time was 22 min). However, it was found that decreasing the bed height will decrease the breakthrough time (at H = 5 cm, breakthrough time was 9 min while at H=20 cm, breakthrough time was 40 min). The achieved experimental results were different from the ADSIM one. The percentage removal obtained experimentally after 2 hr at 150 mg/L, 10 mL/min and 10 cm was zero. The breakthrough time resulting at initial concentration 100 mg/L, Q = 15 mL/min and 5 cm were 454, 351 and 152 min respectively.

Table of contents

List of Figures

Appendices

List of Tables

Nomenclature

Symbols and units

q	Adsorbed amount (mg/g)
t_B	Breakthrough time
˚C	Celsius
Cm	Centimeter
cm^3	Cubic centimeter
G	Gram
H	Hour
C_0	Initial concentration ($kmol/m^3$)
L	Liter
MTC	Mass transfer coefficient (1/min)
m^2	Meter squared
µm	Micro meter
Mg	Milligram
mL	Milliliter
Mm	Millimeter
Min	Minutes
d_p	Particle diameter (m)
Ppm	Parts per million
S	Seconds
Q	Volumetric flow rate (m^3/s)

% R	Removal efficiency

Abbreviations

AC	Activated carbon
BA	Bagasse ash
COD	Chemical oxygen demand
GAC	Granular activated carbon
HRP	Horseradish peroxidases
OMW	Olive mill wastewater
PAC	Powder activated carbon
PEG	Polyethylene glycol
RCB	Residual coal treated with H_3PO_4
SBP	Soybean peroxidase
T	Temperature
WC	Wood charcoal

Chapter 1: Introduction

1.1 Background

Water scarcity is one of the challenges facing the Palestinian people in particular and the world in general, which related to political and natural conditions. To resolve this problem, the attention turned to wastewater which discharged into the environment. The value of the chemical oxygen demand (COD) of wastewater in one of the Palestinian areas was ~995 mg/L ("Monthly treatment plant work report," 2019) that indicates the need for treatment before discharge to minimize the pollution potential. Thus, the idea of wastewater treatment came to reduce these values and get rid of the toxins. Thus, maintain a green environment and on the other hand provide another source of water in the areas suffering from scarcity.

Human waste, food scraps, oils, soaps and chemicals are substances that may present in wastewater. Which are toxic to humans, animals, and the environment. However, some organic compounds as phenolic-based compounds (phenol, chlorophenols, cresols, aniline, resins and alkylphenols) may be very toxic even at low concentrations (Anku et al., 2017). The physical and chemical property, reactivity and stability, and how to handle with phenol is illustrated in the **Material data sheet of phenol (MSDS)** in appendix A. Therefore, there is an essential need to get rid of phenolic compounds. These techniques include activated carbon adsorption, solvent extraction, ozonation, photocatalytic degradation, biological treatment, electro-Fenton, ion exchange, membrane-based separation, and photodecomposition (Anku et al., 2017). Adsorption provides considerable efficiency, simple design, easy to operate, cost-effective, and the ability to control pollutants (Crini et al., 2018).

The selection of the appropriate adsorbent is one of the essential things to consider in adsorption. The most conventional adsorbents used in the adsorption of phenol are zeolite, activated carbon (AC), bagasse ash, resin, and modified alumina (Anisuzzaman et al., 2016) (Anku et al., 2017). However, AC is considered the most common one and has the ability to adsorb phenol; its efficiency reaches 98% (Mukherjee et al., 2007). This is due to the large surface area and its structure.

1.2 Aspen adsorption program (ADSIM)

Aspen adsorption simulation (ADSIM) is a process simulation software, it provides several flow sheets. Where you can achieve the optimal design, the best simulation, and analysis for both gas and liquid adsorption process. ADSIM helps in a better understanding of the processes through accurate rate-based adsorbent bed designs. Where several geometries including axial column, horizontal and radial beds are available (Aspentech, 2019). The software contains a wide range of isotherm models such as Freundlich, Langmuir, and stoichiometric equilibrium. Moreover, several choices of kinetic models as lumped resistance and micro/macro-pore. To complete the processes in ADSIM, Aspen properties database is used. Indeed, it is the largest physical property database. ADSIM provides more than 36 training examples with summarized instructions, which can help in starting adsorption simulation (Tech, 2019).

1.3 Problem statement

Phenolic compounds are released to the environment through the industrial, domestic, agricultural and municipal discharge (Anku et al., 2017). Where phenol may exist in the effluent of several industries as coal processing (9 - 6800 mg/l), manufacture of petrochemicals (2.8 - 1220 mg/l), coking operations (28 - 3900 mg/l), refineries (6 - 500 mg/l), pharmaceutical, paint, pulp and paper industries (0.1 - 1600 mg/l) (Busca et al., 2008). These industrial plants do not design units for the treatment of resulting phenol, to minimize their effect. The phenolic compounds have a high ability to react, which allows them to react with different inorganic substances and microorganisms and form high toxicants (Anku et al., 2017). Phenol is classified as a toxic substance for humans through inhalation, oral or dermal exposure. Moreover, it can cause skin burning, genetic and oregano defects. Its water solubility at 25 ^{o}C magnitudes 80 g/l. So, the disposal of effluent contains phenol must be done in a proper way (sasoltechdata.com, 2014). United states environmental protection agency (EPA) considers 1 mg/l as the maximum allowable concentration in wastewater effluents (El-Naas et al., 2017).

1.4 Research objectives

This research project targets to applying an experiment data for the adsorption of phenol using AC in a packed-bed column to the ADSIM software, and comparing the result obtained from the experiment with the result obtained from ADSIM. This is to know the accuracy and efficiency of the ADSIM. Also, it aims at reducing the concentration of phenol in the effluents of wastewater to a certain concentration, which was legislated by EPA (less than 1 mg/L).

1.5 Scope of this work

In this study, the adsorption of phenol from wastewater using AC in a packed-bed column was investigated by ADSIM, which used to simulate the process. The effect of different parameters: the inlet concentration of phenol, inlet liquid flow rate, column height and particle size of the adsorbent (AC) were studied to determine the effect of changing these parameters on the adsorption process (Breakthrough and saturation time). The study was started by applying an experiment from literature in ADSIM with a list of assumptions: isotherm, kinetic model, discretization method, mass and energy balances.

1.6 Importance of this work

This project will bring many benefits, most notably: minimize the discharged polluting phenol to the environment. Besides, this project targets linking the simulation program and the experimental work. To the author’s knowledge, this linking approach is conducted for the first time.

1.7 Organization of the report

This project consists of six chapters: Chapter 1 provides information about the state of water and wastewater in Palestine. Also, it shows the pollutants that may exist in wastewater. Moreover, it explains the toxicity of phenol and techniques used to treat phenol from wastewater. Adsorption of phenol and adsorbent also is discussed in this chapter. Additionally, the problem statement, the objectives of the research and the scope of work are presented in this chapter. Chapter 2 shows the faced constraints and engineering standards. Chapter 3 presents a state of the literature review for previous researches related to this project and their findings. Chapter 4 explains the methodology and the materials used in this project. The experimental works are illustrated in Chapter 5. The obtained results are displayed in Chapter 6. In Chapter 7, the result obtained were discussed. The conclusion and some recommendation were presented in Chapter 8.

Chapter 2: Constraints and standards

2.1 Constraints

Experimentally speaking, handling with phenol was overcome by specific safety procedures, where the personal protective equipment: gloves, goggles, lab coat, and closed shoes were dressed to avoid contact with skin, eyes, and clothing. Moreover, the process of preparing different concentrations was done in the fume hood space. The tightly closed, labeled samples were placed away from the hot surfaces and sources of ignition. Theoretically speaking, dealing with ADSIM software was one of the major constraints of the project. This is due to the lack of information needed for the simulation that was not mentioned in the software manual. Thus, a self-learning approach from open access literature from Google and YouTube alongside the proper mentorship of the supervisors has adapted accordingly.

2.2 Standards

Dealing with phenol should be within the standard operating procedure in addition to the personal protective equipment that should be taken into consideration. According to the EPA regulations, the maximum acceptable concentration of phenol in wastewater should be less than is 1 mg/L.

Chapter 3: Literature review

It consists of two parts, **3.1** presents the experimental work done on the adsorption of phenol in a batch and Continuous system. Where **3.2** shows the Aspen work done on this topic.

3.1 Experimental work

Phenolic compounds exhibit serious toxicity if they present in wastewater effluents, even at low concentrations. These compounds considered one of the substances capable of causing cancer, damage to the human organs (kidney, liver, and heart). Moreover, if they exist in a place that contains microorganisms, organic and inorganic compounds; they may interact and produce toxic end-products. Due to its high toxicity, it received a lot of attention. Several types of research studied the treatment of phenolic compounds for more than 15 years. In this chapter, the techniques and attempts used to minimize phenol concentrations in wastewater will be discussed.

In 2005, batch and column experiments were used to remove phenol with a concentration equal to 1000 mg/L from synthetic wastewater using different adsorbents, namely; AC, unmodified residual coal, modified residual coal with H_3PO_4 (RCP), coke breeze and others). In addition, the researchers (Ahmaruzzaman et al., 2005) studied the effect of pH and temperature on the adsorption process. Moreover, the isotherm and the kinetic models of the removal of phenol were addressed. It was found that column capacity was higher than batch capacity for the different adsorbents, for example, the adsorption capacity using AC in batch and column systems were 322.5 and 354 mg/g, respectively. The pH was highly affected by the adsorption capacity, for coal and AC; the adsorption of the phenolic compound was perfectly at their surface (due to its acidic pH). The uptake was decreased by increasing the temperature, the equilibrium data fitted Redlich-Peterson isotherm model and the kinetics model followed the first-order expression. RCP gave the best results for the adsorption of phenol, it was found that RCP was 48% efficient than AC (Ahmaruzzaman et al., 2005).

A comparison between horseradish peroxidases (HRP) and soybean peroxidase (SBP) enzymes for removing phenol from wastewater at the same operation condition (pH: 7.0, temperature 30.0 ^{o}C) was done. Additives with different concentrations used to optimize their performance. It was found that HPR had a removal efficiency higher than SBP at the same pH value (pH = 7.0, the removal efficiency for HRP and SBP were 85% and 38%; respectively). The removal efficiency at T = 30.0 ^{o}C for HRP and SBP was 85 and 38%. HRP was more efficient to remove phenol than SBP, but HRP was more susceptible to deactivation, and it was better protected by polyethylene glycol PEG to avoid the deactivation. It was found that when 0.05 g/L PEG added to HRP, the removal efficiency increased from 22% to 44%, while the same amount of PEG increased the removal efficiency of SBP from 22% to 31%. When the concentration of PEG was increased the removal efficiency was doubled (Bódalo et al., 2006).

The adsorption of phenol from synthetic solution through AC, bagasse ash (BA) and wood charcoal (WC) in a batch system examined by Mukherjee et al. Moreover, the isotherm and kinetics study was addressed. The study was done with two initial concentrations of phenol (30 and 50 mg/l) with 50 g/l of adsorbent dose. In addition, the effect of pH and the presence of nitrate ion and EDTA in the solution were studied. It was found that, the use of BA and WC as adsorbent were inexpensive compared to AC but with less efficiency (removal efficiencies of AC, WC and BA were 98, 90 and 90%; respectively). Also, the Freundlich model was fitted with the adsorption of phenol using AC, BA and WC. The experimental data fitted first-order kinetics model. The presence of nitrate ion and EDTA in the solution was insignificant. The removal of phenol using AC was slightly affected by the pH, while WC and BA were affected at pH higher than 7 (Mukherjee et al., 2007).

(Alhamed, 2009) studied the adsorption of phenol in a packed-bed column using AC, the adsorption kinetics, and the performance of a packed-bed column were studied. The study was carried using different particle sizes (0.45, 0.8, and 1.5 mm), the heights of the bed used in the study were 5, 10, 15, 20, and 25 cm. The initial concentrations of phenol were 200 and 400 ppm and the flow rates were varied from 23.3 to 141.5 ml/min. The outcomes of the study were revealed that adsorption kinetics followed the pseudo-second-order model, the larger particle size of AC indicated significant intraparticle mass transfer resistance. Thus, the rate of adsorption was decreased with the increase of AC particle size. Also, that experimental data was fitted the model data with longer bed height and lower flow rate.

Palestine is known with high olive oil production level, which leads to high (OMW). Therefore, the removal of polyphenols from OMW using activated olive stones (AOLS) as an adsorbent in Palestine was investigated. The ALOS was synthesized from the olive stones and potassium hydroxide KOH as an activating agent. The prepared adsorbent had high microspores with a surface area equals to 368.3 m^2/g. The process was done within a fixed-bed column and obtained around 50.0% removal efficiency of OMW (Aladham, 2012).

In 2013, the adsorption of phenol from industrial wastewater using olive mill solid waste, which was washed, dried, crushed and sieved has been also conducted. The test was done in batch and continuous processes at a fixed temperature of 25 ^oC. In the batch process, the operating time, initial phenol concentration (50 - 700 mg/L) and solid to solution ratio varied to determine their effect on the adsorption process. While in the column process, bed height (0.2 m), flow rate (0.2 - 0.6 cm^3/s) and initial phenol concentration (250 mg/L) were varied. It was found that olive mill solid waste was a good selection adsorbent for the adsorption of phenol from aqueous solutions. The removal efficiency was increased from 52.0% to 85.0% when the adsorbent dosage was changed from 0.25 to 1.0 g/L. In addition, as the flow rate, initial concentration, and bed height were increased, the adsorption rate was increased. While as flow rate was decreased, the rate of adsorption was increased. The experimental data were fitted to the Dubinin-Radushkevich isotherm model and the kinetics were following the pseudo-second-order (Abdelkreem, 2013).

In 2014, a treatment of olive mill based wastewater using conventional magnetic (γ-Fe_2O_3) nanoparticles for dephenolization (phenol removing) from synthetic and diluted real OMW. The study confirmed that γ-Fe_2O_3 nanoparticles succeeded to achieve a high adsorption rate of phenol, where the adsorption equilibrium was carried out at less than 10.0 min for real OMW with 100 mg/L of phenol. Unlike the conventional methods where AC and activated alumina are used and needed several days to reach the adsorption equilibrium. Moreover, it was found that the phenol adsorption from wastewater by the γ-Fe_2O_3 nanoparticles is pH-independent (Nassar et al., 2014).

In (Girish et al., 2014), the adsorption of phenol from aqueous solution using AC was studied in a Packed Bed column. Moreover, the performance of the adsorption process was predicated using different models. Such as Thomas, Adams-Bohart, Yoon Nelson, Modified dose–response and linear driving force model LDFQ. Also, the effect of different variables on breakthrough curves were investigated in this study. It was found that the best models to predict the performance of the process were Thomas and LDFQ. AC were suitable adsorbent for the removal of phenol. The result showing that as the initial concentration and the bed height increased, the removal efficiency increased. However, %R were declined as the flowrate ascended.

Sklavos et al. treated OMW using solar distillation. This process recovered the phenolic compounds, through 16 days of experiments. The results showed that the pH and COD concentration in the distillate was gradually lowered during the experiment (1^{st} day: pH = 5.07 and the last day: pH = 3.40, 1^{st} day: COD = 31000 mg/L and the last day: COD = 4800 mg/L). While, an increase in the conductivity and total phenol concentration were noticed (during 10 days: total phenol concentration = 1.5 mg/L, after 6 days: total phenol concentration: 4.3 mg/L. In addition, using thermal insulation enhanced the performance of the solar distillation treatment process (Sklavos et al., 2015).

In 2017, the adsorption of phenol from petroleum refinery wastewater onto AC was studied in a packed-bed column. In addition, the relation between the uptake of phenol and the operating conditions were studied. AC within the packed-bed column was showed high efficiency in the removal of phenol. In addition, flow rate, feed concentration and amount of packing were influenced the performance of the packed-bed column. The bed had better performance at low inlet concentration, low flow rate and high amount of packing. The experimental data fitted to the Langmuir model.

In 2017, a designed for a packed bed column was done based on laboratory scale for the adsorption of phenol using modified coal fly ash (MCFA). The breakthrough time was found 113.98 min while the contact time was found 10.6 min. The designed parameters for the adsorption column were as following; the column area was 117.75 cm^2 and12.2435 cm for the bed diameter with flow rate equal to 150 cm^3/min. The required amount of MCFA was 3338.17 g (Chauhan et al., 2017).

In 2018, another study was tested the adsorption of phenol by a rotary packed-bed reactor using AC. The effect of gravity factor (varied from 0.0 to 79.0), initial phenol concentration, and the liquid spray density on the adsorption process were investigated (Li et al., 2018). It was noted that the adsorption amount in the rotating packed-bed was much higher than the conventional packed-bed (rotating bed: 32.27 mg/g while in conventional packed bed 22.44 mg/g). When the gravity factor was increased to 44.68, the adsorption amount was increased from 0.0 to ~27.0 mg/g. The variation of the liquid spray density was from 1.04 to 1.46 $m^3/m^2.h$, was increased the adsorption amount from 29.71 to 32.27 mg/g. Moreover, it has been found that the Freundlich model exhibited the best performance (Li et al., 2018).

Garlic peel used as eco- friendly and cost effective adsorbents in (Muthamilselvi et al., 2018) for phenol removal. The effect of operating parameters was studied, such as the inlet flowrate at (10, 15 and 25 ml/min), 15 cm bed height and 50 mg/l initial concentration. It found that the breakthrough time decreased with increasing the flowrate. The breakthrough time was 160, 90 and 40 min at 15, 20 and 25 ml/min flowrate respectively. It indicated that improving the efficiency of the utilization of garlic peel is possible at low flowrates since this will maintain the performance for a longer time within breakthrough levels with a higher specific rate of adsorption. In addition, models of continuous column adsorption such as Thomas model, Yoon-Nelson, Adams- Bohart and Clark models studied. The Yoon-Nelson model was applicable model for the adsorption of phenol by garlic peel.

3.2 Aspen simulation

The Aspen adsorption used to investigate the feasibility of AC in phenol adsorption process in (Krishnaiah et al., 2014). The material balance assumptions in aspen adsorption contains several options. A comparison between the convection and the convection with estimated dispersion models was done. It found that the convection with estimate dispersion model is faster to achieve the equilibrium. Moreover, a comparison for the inlet flowrate applied in the simulation. It found that higher uptake values observed at lower flowrate while the breakthrough occurred faster at higher flowrate.

A study on dynamic simulation of phenol using AC by a packed-bed column was done in 2016. ADSIM software package was used to simulate the process. The effect of initial phenol concentration, inlet liquid flow rate, column height and particle size on the phenol adsorption were examined. The outcomes were revealed that as the column height increased, the breakthrough time and the saturation time extended. On the other hand, the effect of particle size was not significant. Moreover, the inlet liquid flow rate and the breakthrough time have a proportional relation. According to the ADSIM simulation results, the adsorption column was not feasible for conventional water treatment plant (Anisuzzaman et al., 2016).

Chapter 4: Materials and methods

4.1 Adsorbate

Phenol (C_6H_6O or C_6H_5OH) is an aromatic organic compound and known as carbolic acid. Its molecular weight is 94.11 g/mol and its boiling and melting points are 181.75 °C at 101.3 kPa and 41.0 °C, respectively. Phenol has a density equal to 1.07 g/cm³, and has an absorbance at a maximum wavelength (λ_{max}) of 268 nm.

Phenol with 90.0% purity, was commercially available from Chen Samuel Chemicals (Haifa Bay, Haifa, and used as received in the laboratory. In addition, deionized water was used without further purification.

4.2 Adsorbent

AC from lantana camara was used in this study; the particle size was 11.59 µm. AC has a bulk density equals to 0.74 g/cm³ with porosity equals to 0.427. The inter-particle and intra-particle voidages are 0.5 m^3 void/m^3 bed and 0.6 m^3 void/m^3 bead, respectively.

4.3 Adsorption parameter estimation:

- Breakthrough curve: It is obtained by plotting the ratio of the effluent and initial concentration versus volume treated or time of treatment.
- Breakthrough time t_B: Is the time needed for the outlet concentration to reach 10 % of initial concentration . **Figure 1** showing the breakthrough curve and the breakthrough time.

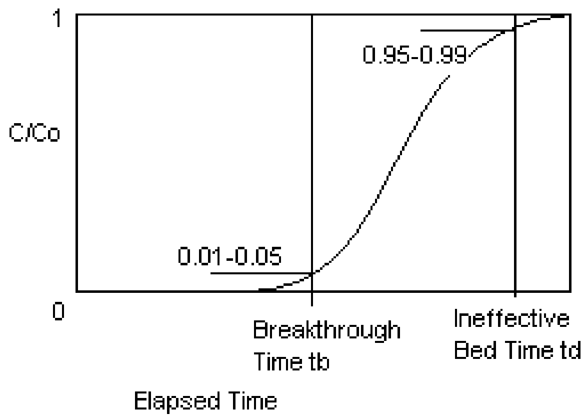


Figure 1: Breakthrough curve and time.

Where t_B is obtained at :

$$t_B = 0.01\ \frac{C}{C_0}$$

Where:

C_0: Initial concentration in mg/L.

C: The concentration at the effluent of the column in mg/L.

- Removal efficiency %R: The total phenol removed with respect to the phenol feed entering the column which given by:

$$\%R = \frac{C_0 - C}{C_0}$$

4.4 Modeling the column data

The prediction of breakthrough curve is important in the design of an adsorption column. Many models have been developed for illustrating the column behavior and performance, This model are Thomas, Adams-Bohart, Yoon Nelson, Modified dose–response, linear driving force model based on fluid phase concentration difference (LDFC) and linear driving force model based on particle phase concentration difference (LDFQ). According to (Girish et al., 2014) LDFC model was a good model to predict the breakthrough curves for the adsorption of phenol.

Linear driving force model based on fluid phase concentration difference (LDFC):

The LDFC model is applied when the fluid phase concentration difference is the driving force for adsorption process. It is also based on the fact that mass transfer from the fluid phase to the solid surface dominates the process. The expression is as follows:

$$t = t_0 + \frac{\rho_b \; q_0 C_o}{k_f}(1 - \frac{Rln(1-x) - lnx}{1-R})$$

Where:

t_0: The characteristic time (min).

ρ_b: The bulk density of bed (g /cm^3).

q_0: The solid phase concentration in equilibrium with C_0 in mg/g.

k_f: The fluid-to-particle mass transfer coefficient concentration

R: Equilibrium parameter.

x : The dimensionless outlet concentration.

$$R = \frac{1}{1 + bC_0}$$

b: The Langmuir constant (L/mg).

4.5 Theoretical simulation

Aspen Adsorption V9.1 and Aspen property V9.1 simulation programs were used to simulate the adsorption of phenol by AC from wastewater. (Girish et al., 2014) applied the adsorption of phenol experimentally using AC as an adsorbent in a packed-bed that was used as step-stone sources for the experimental data. Here are the list of assumptions used for the dynamic adsorption process:

1. Mass/momentum balance.
2. Energy balance: Isothermal.
3. Kinetics model: Linear lumped resistance.
4. Discretization method: Upwind differencing scheme 1 (UDS 1).
5. Adsorption isotherm: Langmuir model (Girish et al., 2014).
6. Pressure drop: None.

7. Velocity: Constant.
8. Film model: Fluid.

The dynamic simulation was run at 28.0 ^{o}C and 1.0 bar. Then, the effect of several parameters such as column height, inlet liquid flow rate and the initial phenol concentration on the breakthrough was determined. The inlet liquid flow rate and phenol concentration were varied as follows; the simulation was started with 10 mL/min as initial liquid flow rate and then this value was changed to (15.0 and 20.0 mL/min) in order to determine their effect on the breakthrough and saturation time. 100 mg/L were fed to the ADSIM as initial phenol concentration, after that this value was varied to (150 and 250 mg/L). This value was changed to specify their effect on both breakthrough and saturation time. The same thing was done with height, starting from 5 cm and then changed to 10 and 15 cm. **Figure 2** describes the methodology, briefly. **Table 1** shows input data, which were inserted into ADSIM.

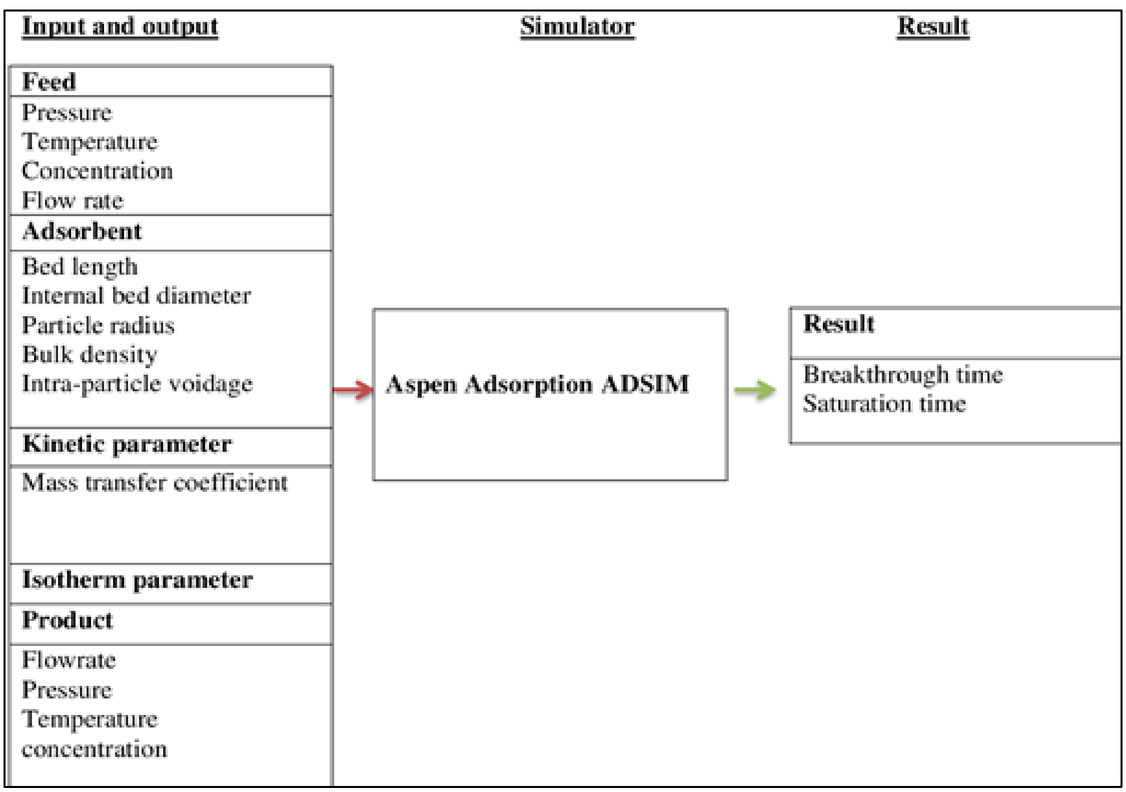


Figure 2: Schematic diagram of the simulation methodology.

Table 1: The values of the model input parameters.

Parameter	Value	Reference
Pressure (bar)	1	(Girish et al., 2014)
Temperature (K)	301.15	(Girish et al., 2014)
Inlet liquid flow rate (mL/min)	10.0, 15.0, 20.0	(Girish et al., 2014)
Concentration of phenol (mg/L)	100, 150, 200	(Girish et al., 2014)
Height of adsorbent layer (cm)	5.0, 10.0, 15.0	(Girish et al., 2014)
Internal diameter of the adsorbent layer (cm)	2	(Girish et al., 2014)
Parameter	Value	Reference
Inter-particle voidage (m^3 void/m^3 bed)	0.5	(Girish et al., 2014)
Intra-particle voidage (m^3 void/m^3 bed)	0.6	(Krishnaiah et al., 2014)
Bulk density of adsorbent (kg/m^3)	740	(Anisuzzaman et al., 2016)
Adsorbent particle radius R_p (m)	5.8×10^{-6}	(Girish et al., 2014)
Isotherm parameter, 1 of phenol (mg/g)	112.5	(Girish et al., 2014)
Isotherm parameter, 2 of phenol (1/mg)	0.03951	(Girish et al., 2014)

Chapter 5: Experimental and simulation works

5.1 Experimental works:

In the first stage of the second part of the project, a practical experiments were planned to be conducted in order to find all information necessary to operate the adsorption process in the laboratory. The planned was to do experiments to find the mass transfer coefficient and isotherm parameters. The column was designed for the adsorption process and was sent to the glassware workshop to implement it, it was equipped and the adsorption process was going to start in the lab. But due to the circumstances, our plans were not completed.

- **Calibration curve**

A stock solution with a concentration equals to ~140 mg/L was prepared by dissolving 0.16 g of liquid phenol in 1.0 L of deionized water. The stock solution was diluted to obtain solutions with 75.0, 50.0, and 25.0 mg/L. The required amounts were withdrawn from the stock solution. The detailed calculations are shown in **ADSIM procedure**:

The following steps show the Aspen procedure that was considered for simulation in this project:

1. The program was opened; the components were inserted to the component list as shown in **Figure A 8**, where Aspen property system was used for the physical property configuration.

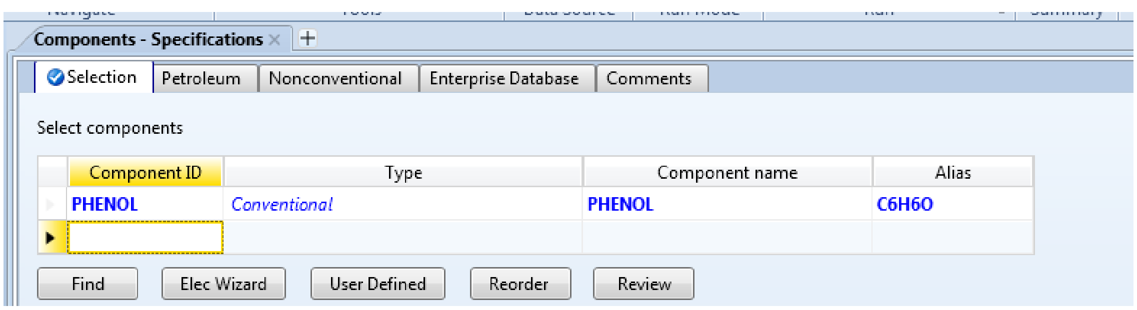


Figure A 8: Aspen components list.

2. The appropriate property method was specified, PENG-ROB as shown in **Figure A 9** below.

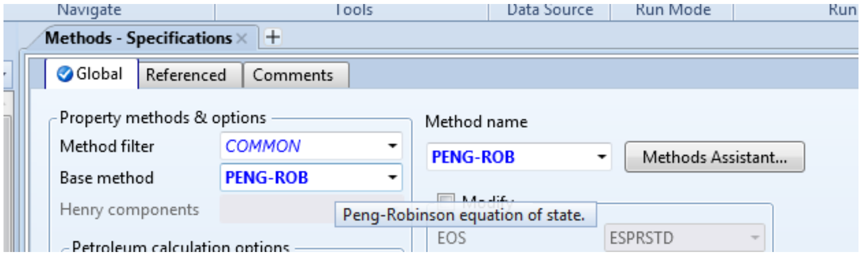


Figure A 9: Aspen property method.

3. After that, the system was run, and the property document was saved as PropsPlus.aprbkp**.** The green square, which was shown in **Figure A** 10, means that the properties are successfully configured in the properties configuration form.

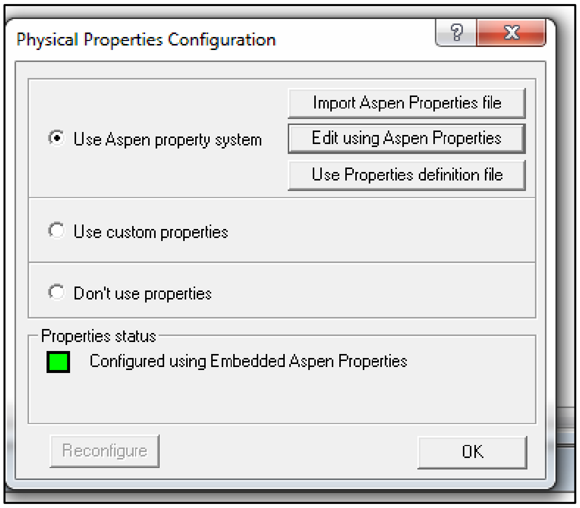


Figure A 10: Physical properties configuration.

4. The process was created as shown in **Figure A** 11 by adding the liquid feed, liquid bed and liquid product from (library-ADSIM) to the flowsheet and connected to each other using the connection.

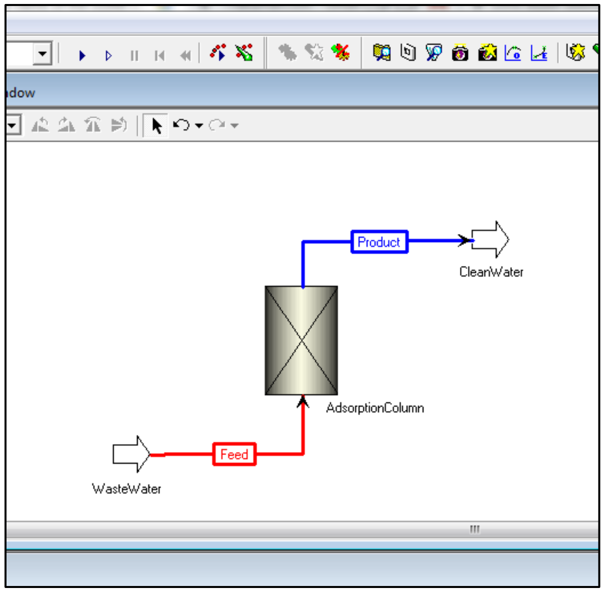
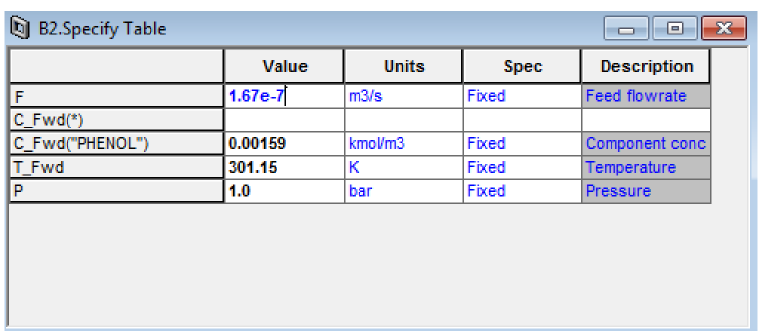


Figure A 11: Adsorption process flowsheet.

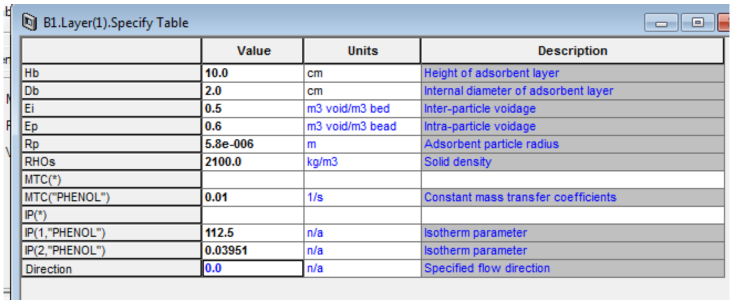
5. Operating parameters; flow rate, concentration, temperature and pressure were inserted for the feed stream by double click on the liquid feed. The same for the liquid product. **Figure A 12** shows the liquid feed configuration


B2.Specify Table

	Value	Units	Spec	Description
F	1.67e-7	m3/s	Fixed	Feed flowrate
C_Fwd(*)				
C_Fwd("PHENOL")	0.00159	kmol/m3	Fixed	Component conc
T_Fwd	301.15	K	Fixed	Temperature
P	1.0	bar	Fixed	Pressure

Figure A 12: Liquid feed (wastewater) configurations.

6. The configurations of the bed were added by double click on the liquid bed as shown in **Figure A 13**.



	Value	Units	Description
Hb	10.0	cm	Height of adsorbent layer
Db	2.0	cm	Internal diameter of adsorbent layer
Ei	0.5	m3 void/m3 bed	Inter-particle voidage
Ep	0.6	m3 void/m3 bead	Intra-particle voidage
Rp	5.8e-006	m	Adsorbent particle radius
RHOs	2100.0	kg/m3	Solid density
MTC(*)			
MTC("PHENOL")	0.01	1/s	Constant mass transfer coefficients
IP(*)			
IP(1,"PHENOL")	112.5	n/a	Isotherm parameter
IP(2,"PHENOL")	0.03951	n/a	Isotherm parameter
Direction	0.0	n/a	Specified flow direction

Figure A 13: Liquid bed configuration.

7. The simulation was run to get the breakthrough curve as shown in **Figure A 14**.

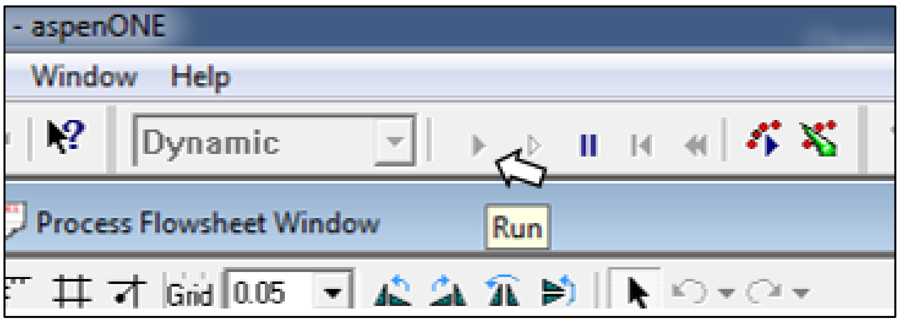


Figure A 14: Simulation run.

➢ **MTC estimation:**

Mass transfer coefficient (MTC):

The MTC was calculated by aspen, by following the steps below.

1. 0.01 (1/min) was inserted to liquid bed configuration in ADSIM as an initial guess for MTC value (**Figure A15**).

	Value	Units	Description
Hb	10.0	cm	Height of adsorbent layer
Db	2.0	cm	Internal diameter of adsorbent layer
Ei	0.5	m3 void/m3 bed	Inter-particle voidage
Ep	0.6	m3 void/m3 bead	Intra-particle voidage
Rp	5.8e-006	m	Adsorbent particle radius
RHOs	2100.0	kg/m3	Solid density
MTC(*)			
MTC("PHENOL")	0.01	1/min	Constant mass transfer coefficients
IP(*)			
IP(1,"PHENOL")	112.5	n/a	Isotherm parameter
IP(2,"PHENOL")	0.03951	n/a	Isotherm parameter
Direction	0.0	n/a	Specified flow direction

Figure A15 : Initial guess for MTC value.

2. The concentration of phenol at several times (**Table A 1**) was calculated from experimental breakthrough curves (**Figure A 16**).

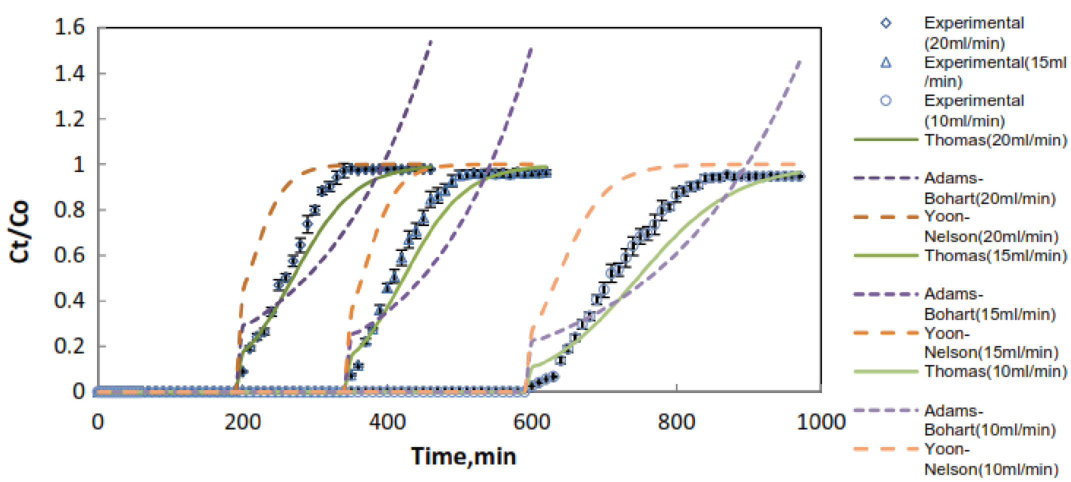


Figure A 16: Experimental breakthrough curve at 150mg/l concentration and 10 cm bed height.

Table A 1: The required data for MTC calculations.

C_0 (mg/l)	150	
C_0 (mol/l)	$1.594e^{-6}$	
Q(ml/min)	20	
time	**C/C0**	**C**
200	0	0

250	0.35	0.000558
300	0.8	0.001275
350	0.95	0.001514
400	1	0.001594

The next steps were available at the following links:

https://www.youtube.com/watch?v=Pr5CyXpdgxY

https://www.youtube.com/watch?v=KmH7XGtkhTM.

Appendix B. The calibration curve was constructed following these steps:

1. A sample was taken from one of the standard solutions and placed in the cuvette, and then put in the UV-Vis spectroscopy to obtain the absorbance peak at 268 nm.
2. Then, samples with different concentrations were taken from each standard solution and replaced in the UV-Vis spectroscopy. The corresponding absorbance values for each concentration were recorded and the calibration curve was then constructed.

➢ **Isotherm parameters:**

Batch adsorption techniques were carried out to find the isotherm parameters of phenol at lab temperature. A stock solution of 500 ppm phenol concentration was prepared in the hood. Then, another five samples with different concentrations were set by diluting the stock solution. Six volumetric flasks of 500, 400, 350, 300, 250, and 200 ppm phenol concentration were ready. 10 ml of each concentration was withdrawn and put in small tubes with 0.1 g of AC. All tubes were put in the shaker at the same time for two hours. After the shaking process, the tubes were placed in the centrifuge apparatus for five minutes at 3500 rpm. A clear sample was withdrawn from each tube and placed in the cuvette for the screening test in the UV- spectrometer.

5.2 Aspen property method

To run the ADSIM simulation correctly, the suitable method must be used. According to (Krishnaiah et al., 2014) The selected process was **PENG-ROB**. Usually, the following diagram (**Figure 3**) is used to find the proper method.

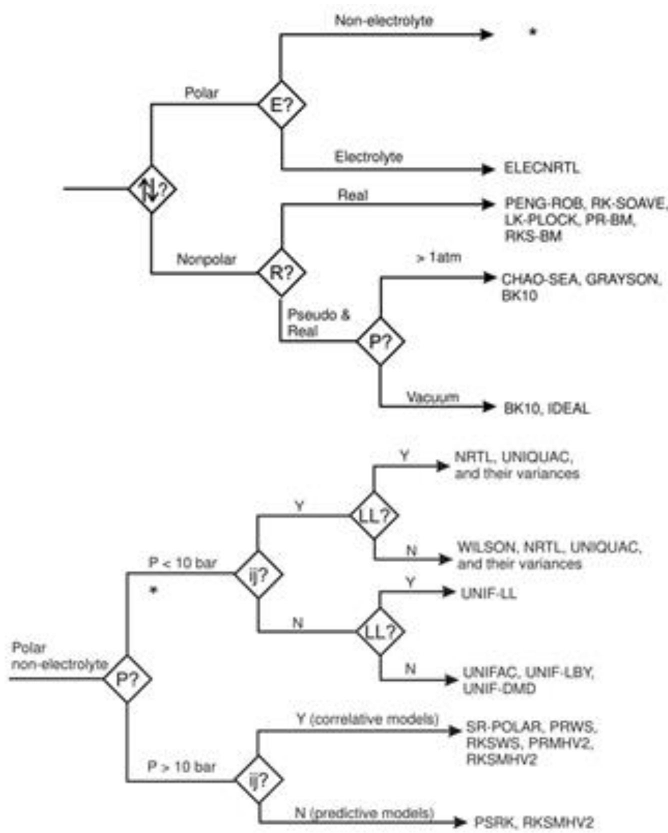


Figure 3: Guidelines for choosing a property method.

5.3 Aspen procedures

The steps which were as per following in ADSIM and were presented in **Appendix A.**

Chapter 6: Result and Analysis

6.1 Isotherm parameters:

The result obtained from the experiment done was incorrected, the experiment was repeated several times to obtain accurate result . The result was that AC affecting the deionized water, the isotherm parameters were not obtained in lab. As a result of that, isotherm parameters were not estimated.

6.2 Mass transfer coefficient (MTC):

Mass transfer coefficients were estimated by the ADSIM depending on experiment data which were obtained from (Girish et al., 2014) based on the breakthrough curves . **Appendix A** contains the estimation steps in ADSIM, The result obtained were showed in **Table 1**.

Table 2: MTC different values.

C_o (mg/L)	**100**	**150**	**250**
MTC (min^{-1})	0.793	0.605	0.474
Q (mL/min)	**10**	**15**	**20**
MTC (min^{-1})	0.684	0.626	0.556
H (cm)	**5**	**10**	**15**
MTC (min^{-1})	0.505	0.602	0.631

6.2 Effect of Operating Condition

6.2.1 Effect of initial concentration:

The effect of initial concentration on the adsorption process was studied using ADSIM with initial values equal to 100, 150 and 250 mg/L at fixed values for the flowrate and the bed height (15 mL/min and 10 cm), respectively. The resulting breakthrough curve was showing in **Figure 4**. The removal efficiency and the breakthrough time was listed in **Table 3.**

The result showing that as the initial concentration increased, the removal efficiency and the breakthrough time decreased. The result obtained when performing the adsorption process experimentally was represented in **Figure 5** and **Table 4**.

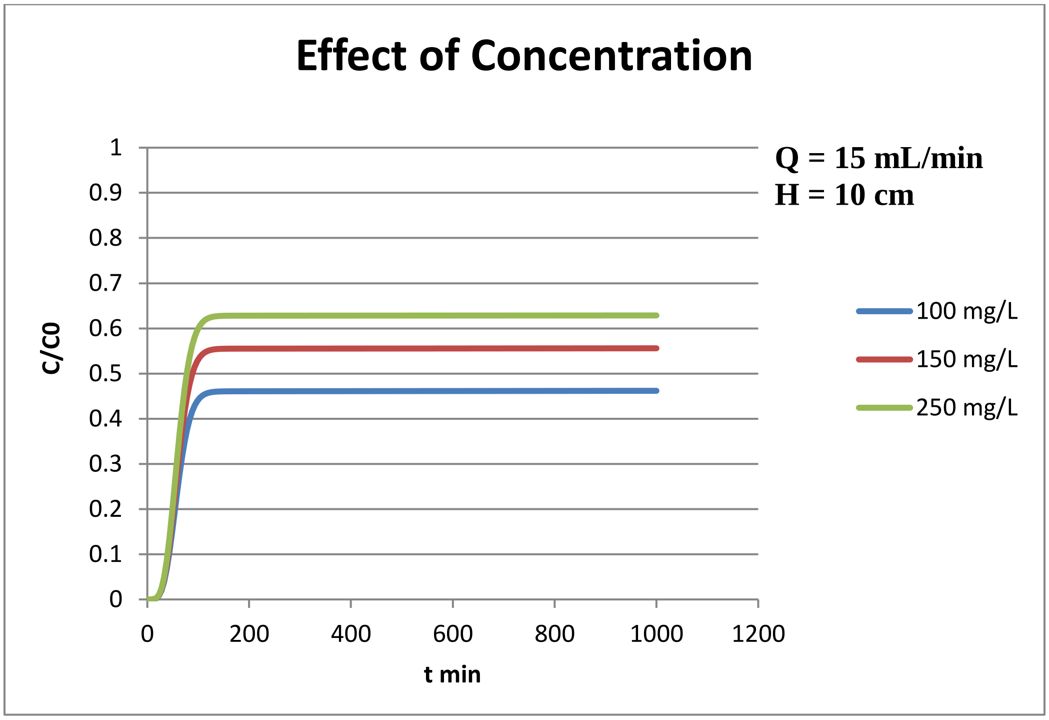


Figure 4: Breakthrough curve obtained from ADSIM at different initial concentration (100, 150, 250 mg/L) and Q =15 mL/min and H = 10 cm.

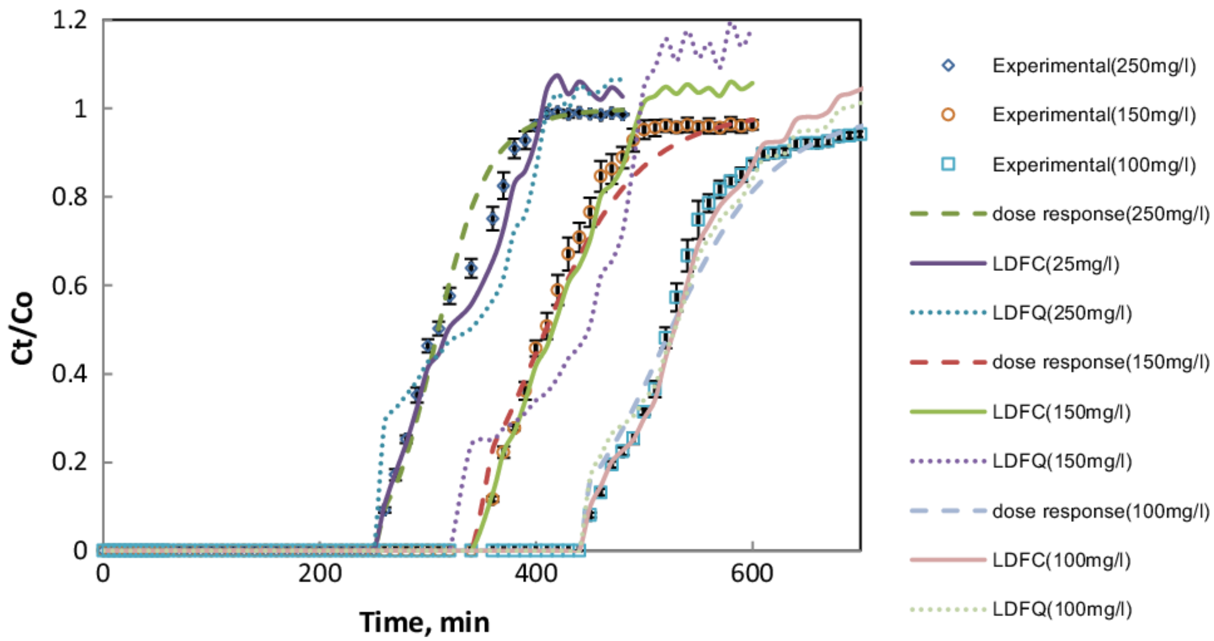


Figure 5: Breakthrough curve obtained from experiment at different initial concentration (100, 150, 250 mg/L) and Q =15 mL/min and H = 10 cm (Girish et al., 2014).

Table 3: The removal efficiency %R and the breakthrough time resulting by ADSIM at different initial concentration.

C_0 (mg/L)	% R after 1 hr	% R after 2 hr	t_B (min)
100	75.1%	54.3%	24
150	70.5%	45%	23
250	67.1%	37.7%	22

Table 4: The removal efficiency %R and the breakthrough time resulting experimentally at different initial concentration (Girish et al., 2014).

C_0 (mg/L)	% R after 1 hr	% R after 2 hr	t_B (min)
100	100	100	454
150	100	100	352
250	100	100	252

6.2.2 Effect of flow rate:

The effect of flow rate on the adsorption process by ADSIM was investigated at different values 10, 15 and 20 mg/L while the concentration and the bed height have these value 150 mg/L and 10 cm, respectively. Breakthrough curve which obtained was showing in **Figure 6**.The removal efficiency and the breakthrough time was figured in **Table 5**.

The result showing that when the flow rate increased, the removal efficiency and the breakthrough time decreased. The obtained result when performing the adsorption process experimentally was represented in **Figure 7** and **Table 6**.

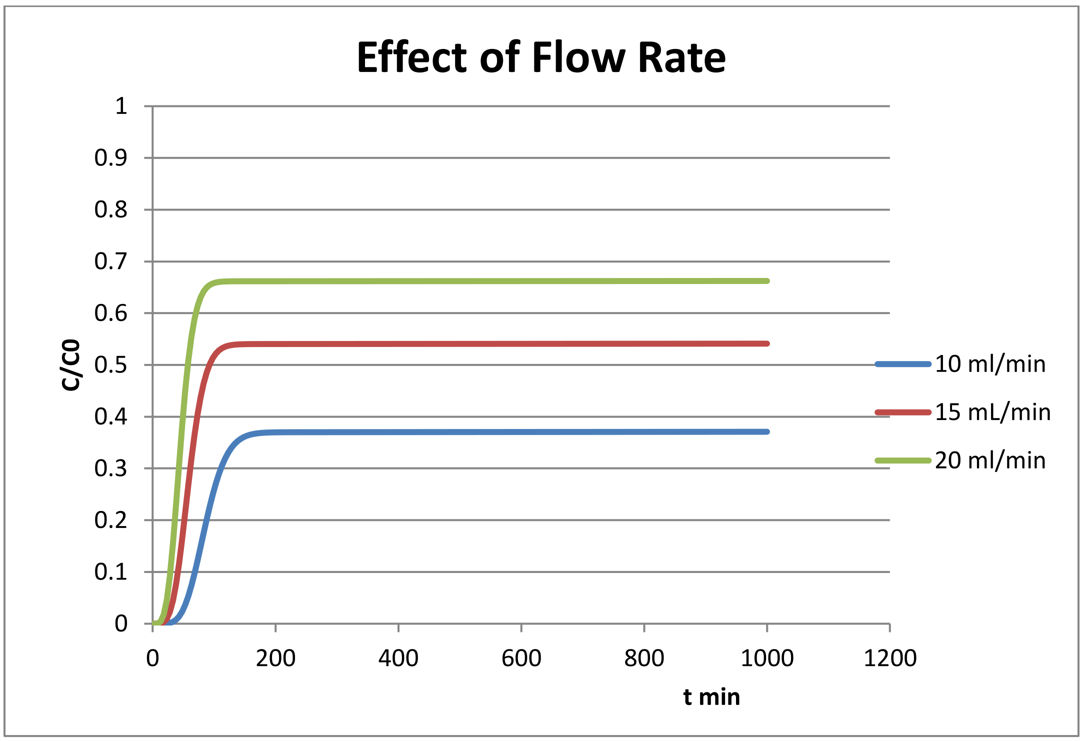


Figure 6: Breakthrough curve obtained from ADSIM at different flow rate (10, 15, 20 mL/min) and C0 =150 mg/Land H = 10 cm.

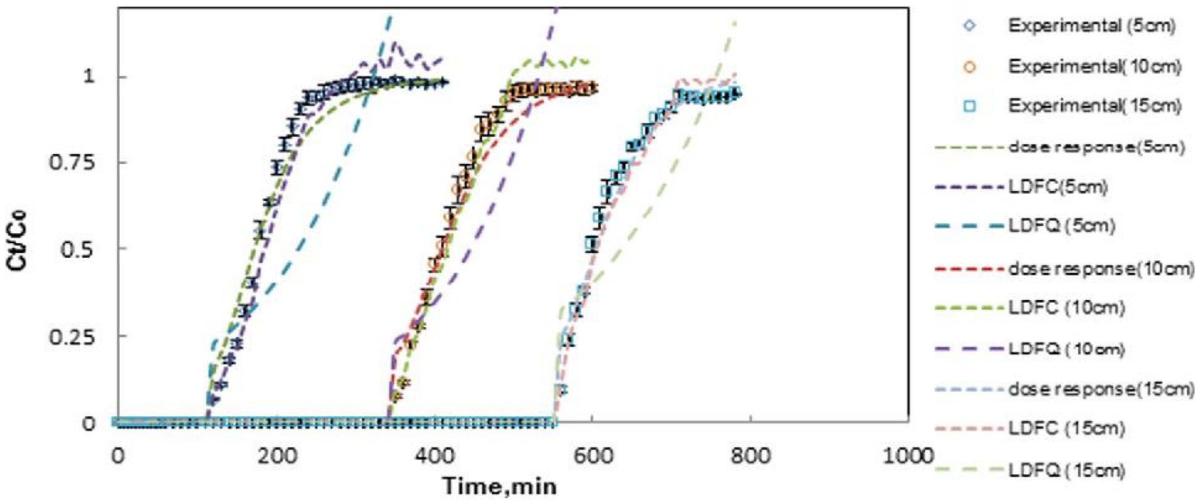


Figure 7: Breakthrough curve obtained from experiment at different flow rate (10, 15, 20 mL/min) and C0 =150 mg/Land H = 10 cm (Girish et al., 2014).

Table 5: The removal efficiency %R and the breakthrough time resulting by ADSIM at different flow rate.

Q (mL/min)	% R after 1 hr	% R after 2 hr	t_B (min)
10	94%	67.6%	40
15	71.3%	46.4%	24
20	47.4%	33.8%	16

Table 6: The removal efficiency %R and the breakthrough time resulting experimentally at different flow rate (Girish et al., 2014).

Q (mL/min)	% R after 1 hr	% R after 2 hr	t_B (min)
10	100	100	604
15	100	100	351
20	100	100	202

6.2.3 Effect of height:

The effect of height on the adsorption of phenol was tested at 5, 10 and 15 cm, while the flowrate and the initial concentration have these value 15 mL/min and 150 mg/L, respectively. Breakthrough curve which obtained was showing in **Figure 8**. The removal efficiency and the breakthrough time was figured in **Table 7**.

The result showing that as the bed height increased, the removal efficiency increased and the breakthrough time increased. The obtained result when performing the adsorption process experimentally was represented in **Figure 9** and **Table 8**.

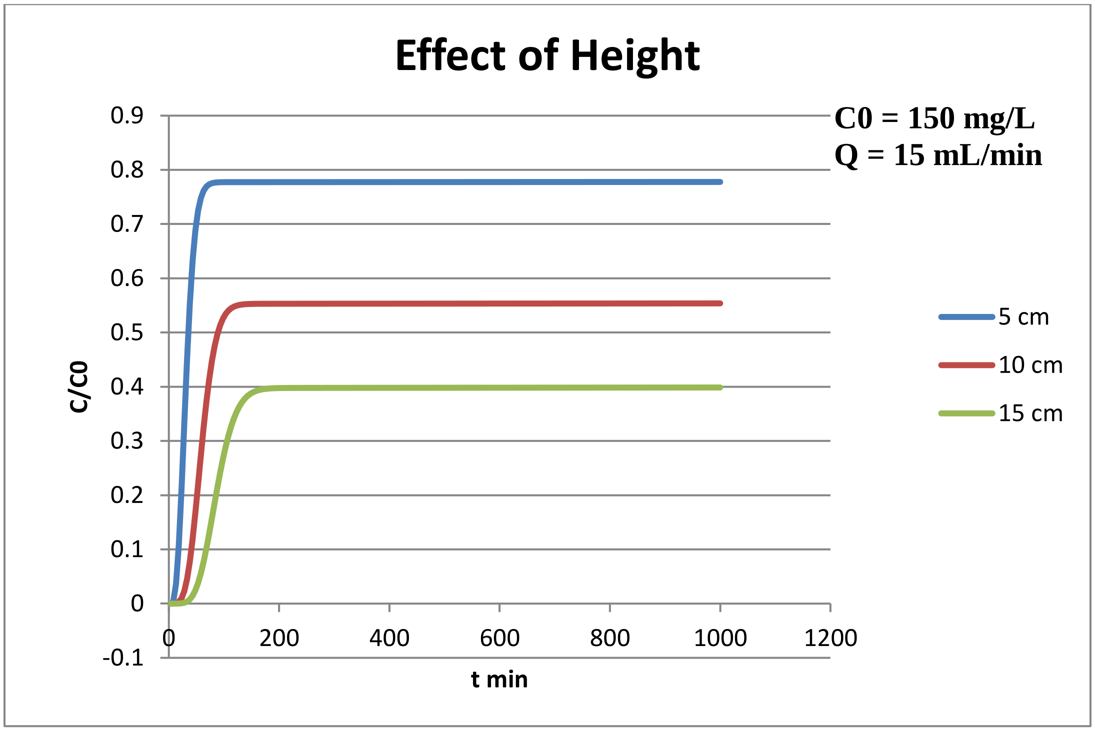


Figure 8: Breakthrough curve obtained from ADSIM at different height (5, 10, 15 cm) and C0 =150 mg/Land Q = 15 mL/min.

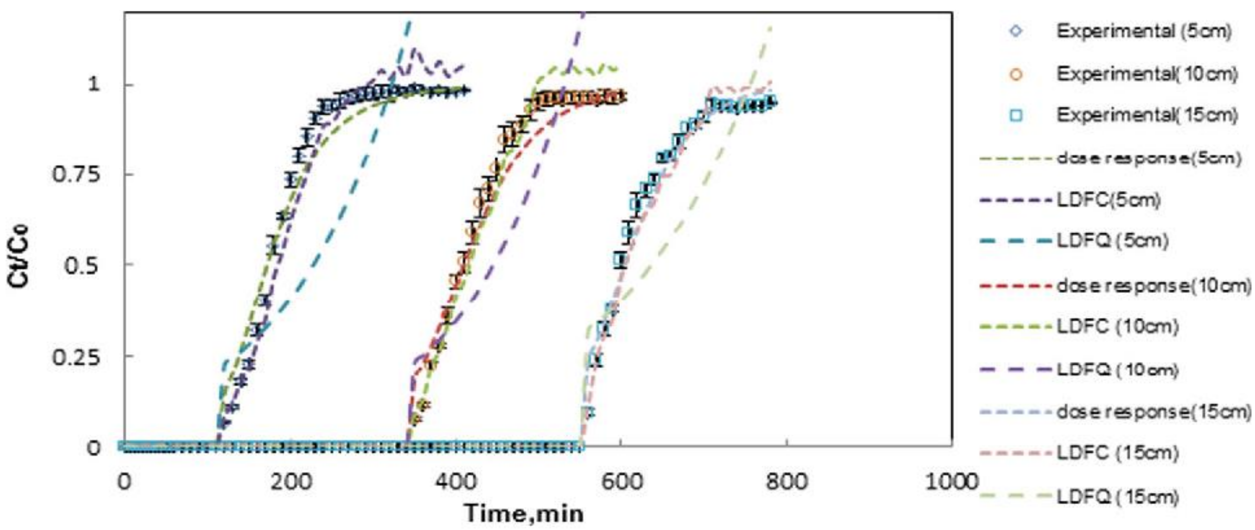


Figure 9: Breakthrough curve obtained from experiment at different height (5, 10, 15 cm) and C0 =150 mg/Land Q = 15 mL/min (Girish et al., 2014).

Table 7: The removal efficiency %R and the breakthrough time resulting by ADSIM at different height.

H (cm)	% R after 1 hr	% R after 2 hr	t_B (min)
5	24.7%	22.3%	9
10	70.7%	45.1%	24
15	93.6%	65.5%	40

Table 8: The removal efficiency %R and the breakthrough time resulting experimentally at different height (Girish et al., 2014).

H (cm)	% R after 1 hr	% R after 2 hr	t_B (min)
5	100	100	152
10	100	100	352
15	100	100	550

Chapter 7: Discussion

The objective of this project was to simulate experiment works that applied the adsorption of phenol in a packed bed column on ADSIM, in order to examine the accuracy of the program and whether it is possible to obtain results similar to the experiment results. In the article (Girish et al., 2014), a practical experiment was conducted, in which the effect of a change the initial concentration C_0, flow rate Q and the bed height H were studied to determine their effect on the removal efficiency and breakthrough time. According to this article, a dynamic simulation depend on the pervious article was run using ADSIM. The simulation was run at 28.0 ^oC and 1.0 bar, the feed data was taken from the article.

The results obtained from the ADSIM were sometimes distinct with the experimental result, whether it is value, increase or decrease. The reason for this was that there is no article containing all the data necessary to run the simulation, which led to the use of an estimation to obtain it or assume it. This data such as mass transfer coefficient, bed characterizations and the assumption adopted. This problem causing the result obtained from ADSIM to be opposite the experimental work. Our project is the first of its kind, as there is no paper in which the adsorption of phenol was experimentally done and applied to the ADSIM. All research is practical except one, therefore, to obtain similar results, an experiment should be done and through it all the variables necessary to run the simulation will be found.

Isotherm parameters were not estimated as a result of incorrect AC work, it was found that AC affected the deionized water which caused the incorrect reading of the UV-Vis spectroscopy. AC may be damaged.

Mass transfer coefficients MTC were not listed in the article, so we were tried to estimate it. ADSIM provides an option to estimate variables. To estimate MTC, experimental dates for each case were fed to the program. This data was taken from the article. For C_0 150 mg/L, MTC was 0.605 min^{-1} while at 250 mg/L it was 0.474 min^{-1}. At Q equal to 10 mL/min, MTC was 0.684 min^{-1} while at 20 mL/min it was 0.55 min^{-1}. The MTC were 0.505 and 0.631 min^{-1} at 5 and 15 cm, respectively.

The effect of initial concentration was inspected at 15 mL/min flowrate and 10 cm bed height constant conditions. The studied concentration values were 250, 100, and 150 mg/L. ADSIM results showed that the breakthrough time decreased when C_0 increased. as a result of the fast saturated of the binding site which is reasonable since the mass transfer driving force increases as the initial phenol concentration increases (Girish et al., 2014). The experimental results showed the same result (decreased) but with different values. In addition to that, the removal efficiency decreased as the initial concentration increased which is opposite to the experimental results. Scientifically, it is decreased due to the insufficient active site.

The experimental results showed the same result (decreased) but with different values. In addition to that, the removal efficiency decreased as the initial concentration increased which is opposite to the experimental results. The result obtained experimentally were the more accurate, Since the driving force increased by increased C_0.

To study the effect of flow rate on phenol adsorption, Q was varying from 5 to 15 mL/min with constant C_0 and H at 150 mg/L and 10 cm, respectively. It can be noticed that the removal efficiency of phenol and the breakthrough time are decreased as the flow rate increased. This was due to decreasing in the residence time which faster the saturation of the column. The same results were obtained experimentally with different values.

In order to study the effect of bed height on the adsorption of phenol. Different adsorption beds H varying from 5 to 15 cm at C_0 150 mg/L and Q 15 mL/min were utilized. The effect of bed height for the uptake of phenol by AC was found to increase by increasing the bed height. Where the percentages of removal of phenol were 24.68%, 70.68% and 93.61% for 5,10 and 15 cm bed height, respectively after 1 hr of adsorption. Moreover, the breakthrough time increased with the increased in bed height. This related to the increasing in the binding sites, which allows more amount of phenol to adsorbed (Girish et al., 2014). The aspen results are similar to the experimental one, even if the values were different.

Chapter 8: Conclusions and Recommendation

The adsorption process of phenol by AC has been studied using ADSIM. Experimental data were applied to make a comparison between the experimental results and what can be obtained by ADSIM. The comparison showed a significant difference in the values between the experimental results and the aspen results. Except that the concept is similar in some cases. Moreover, the impact of various operating parameters was examined such as the initial phenol concentration, flow rate, and bed height. ADSIM has shown that the adsorption capacity decreasing with increases flow rate and influence concentration, but increased with increasing bed height. However, the used article showed that the adsorption capacity increases as the bed depth and influence concentration increase, and decreased with increasing flow rate. Finally, it can be concluded that the present work, discussing an environmental problem, which is the treatment of industrial wastewater. Also, using aspen adsorption as a way to anticipate how effective the project will be.

One of the difficulties faced in our project were the lack of the articles that applied the experimental and simulation work together, which affected the obtained results. Also, we faced the problem of dealing with ADSIM, but it was overcome using the guide of the program.

In spite of all the difficulties we faced, this project added to our experience a lot, as we can now simulate any process. We are now experts in this program. In addition, we learned how to get any information that we lack. This program is a new way to facilitate any treatment process, as it will save time so that the operation of the program will be run and see if desired results are obtained or not.

Recommendations for future work:

The project can come up with more accurate results if an experimental work was done on the lab and same data was utilized in the aspen adsorption. The project can enhance by optimization using ADSIM.

References

Abdelkreem, M. (2013). Adsorption of phenol from industrial wastewater using olive mill waste. *APCBEE procedia, 5*, 349-357.

Ahmaruzzaman, M., & Sharma, D. (2005). Adsorption of phenols from wastewater. *Journal of Colloid and Interface Science, 287*(1), 14-24.

Aladham, R. A. F. (2012). Removal of polyphenols from olive mill wastewater using activated olive stones. *Unpublished Master Thesis). An-Najah National University, Palestine*.

Alhamed, Y. A. (2009). Adsorption kinetics and performance of packed bed adsorber for phenol removal using activated carbon from dates' stones. *Journal of Hazardous Materials, 170*(2-3), 763-770.

Anisuzzaman, S., Bono, A., Krishnaiah, D., & Tan, Y. Z. (2016). A study on dynamic simulation of phenol adsorption in activated carbon packed bed column. *Journal of King Saud university-engineering sciences, 28*(1), 47-55.

Anku, W. W., Mamo, M. A., & Govender, P. P. (2017). Phenolic compounds in water: sources, reactivity, toxicity and treatment methods. *Phenolic compounds-natural sources. Importance and Applications, First Ed. InTech*, 419-443.

Bódalo, A., Gomez, J., Gomez, E., Bastida, J., & Maximo, M. (2006). Comparison of commercial peroxidases for removing phenol from water solutions. *Chemosphere, 63*(4), 626-632.

Busca, G., Berardinelli, S., Resini, C., & Arrighi, L. (2008). Technologies for the removal of phenol from fluid streams: a short review of recent developments. *Journal of Hazardous Materials, 160*(2-3), 265-288.

Chauhan, Y., & Talib, M. (2017). Design of Laboratory Scale Packed bed column for adsorption of phenol on to modified coal fly ash (MCFA). *Int J Sci Eng Technol, 6*(4), 623-625.

Crini, G., Lichtfouse, E., Wilson, L. D., & Morin-Crini, N. (2018). Adsorption-oriented processes using conventional and non-conventional adsorbents for wastewater treatment. In *Green Adsorbents for Pollutant Removal* (pp. 23-71): Springer.

El-Naas, M. H., Alhaija, M. A., & Al-Zuhair, S. (2017). Evaluation of an activated carbon packed bed for the adsorption of phenols from petroleum refinery wastewater. *Environmental Science and Pollution Research, 24*(8), 7511-7520.

Girish, C., & Ramachandra Murty, V. (2014). Adsorption of phenol from aqueous solution using Lantana camara, forest waste: kinetics, isotherm, and thermodynamic studies. *International scholarly research notices, 2014*.

Krishnaiah, D., Anisuzzama, S., Joseph, C., Abang, S., & Siang, L. (2014). Simulation of phenol adsorption in a packed bed column. *Journal of Applied Sciences, 14*(23), 3249-3255.

Li, W., Yan, J., Yan, Z., Song, Y., Jiao, W., Qi, G., & Liu, Y. (2018). Adsorption of phenol by activated carbon in rotating packed bed: Experiment and modeling. *Applied Thermal Engineering, 142*, 760-766.

Monthly treatment plant work report. (2019). Retrieved from http://wwtp.nablus.org/?p=3516

Mukherjee, S., Kumar, S., Misra, A. K., & Fan, M. (2007). Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal. *Chemical Engineering Journal, 129*(1-3), 133-142.

Muthamilselvi, P., Karthikeyan, R., Kapoor, A., & Prabhakar, S. (2018). Continuous fixed-bed studies for adsorptive remediation of phenol by garlic peel powder. *International Journal of Industrial Chemistry, 9*(4), 379-390.

Nassar, N. N., Arar, L. A., Marei, N. N., Ghanim, M. M. A., Dwekat, M. S., & Sawalha, S. H. (2014). Treatment of olive mill based wastewater by means of magnetic nanoparticles: Decolourization, dephenolization and COD removal. *Environmental Nanotechnology, Monitoring & Management, 1*, 14-23.

Sklavos, S., Gatidou, G., Stasinakis, A. S., & Haralambopoulos, D. (2015). Use of solar distillation for olive mill wastewater drying and recovery of polyphenolic compounds. *Journal of environmental management, 162*, 46-52.

Tech, A. (2019). Aspen Adsorption. Retrieved from https://www.aspentech.com/en/products/pages/aspen-adsorption

Appendices:

Appendix A

- ➢ **Material data sheet of phenol**

Safety Data Sheet
according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 03.03.2015 Page 1 of 8

Phenol, Liquified

SECTION 1 : Identification of the substance/mixture and of the supplier

Product name : **Phenol, Liquified**

Manufacturer/Supplier Trade name:

Manufacturer/Supplier Article number: **S25463**

Recommended uses of the product and uses restrictions on use:

Manufacturer Details:

AquaPhoenix Scientific
9 Barnhart Drive, Hanover, PA 17331

Supplier Details:

Fisher Science Education
15 Jet View Drive, Rochester, NY 14624

Emergency telephone number:

Fisher Science Education Emergency Telephone No.: 800-535-5053

SECTION 2 : Hazards identification

Classification of the substance or mixture:

Toxic
Acute toxicity (oral, dermal, inhalation), category 3

Corrosive
Skin corrosion, category 1B
Serious eye damage, category 1

Health hazard
Germ cell mutagenicity, category 2
Specific target organ toxicity following repeated exposure, category 2

Environmentally Damaging
Chronic hazards to the aquatic environment, category 3

Ac. Oral Tox. 3
Aq. ChrTox. 2
Ac. Inhal Tox. 3
Ac. Dermal Tox. 3
Skin Corr. 1B
Eye. Damage 1
Germ Cell
STOT RE 2
Aq. AcTox. 3

Signal word :Danger

Hazard statements:
Toxic if swallowed
Toxic in contact with skin

Created by Global Safety Management, Inc. -Tel: 1-813-435-5161 - www.gsmsds.com

Causes severe skin burns and eye damage
Toxic if inhaled
Suspected of causing genetic defects
May cause damage to organs through prolonged or repeated exposure
Causes serious eye damage
Harmful to aquatic life
Toxic to aquatic life with long lasting effects
Precautionary statements:
If medical advice is needed, have product container or label at hand
Keep out of reach of children
Read label before use
Obtain special instructions before use
Avoid release to the environment
Do not handle until all safety precautions have been read and understood
Do not breathe dust/fume/gas/mist/vapours/spray
Wash skin thoroughly after handling
Do not eat, drink or smoke when using this product
Use only outdoors or in a well-ventilated area
Wear protective gloves/protective clothing/eye protection/face protection
IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician
Collect spillage
Rinse mouth
IF SWALLOWED: Rinse mouth. Do NOT induce vomiting
IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing
Immediately call a POISON CENTER or doctor/physician
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do.
Continue rinsing
IF exposed or concerned: Get medical advice/attention
Take off contaminated clothing and wash before reuse
Store locked up
Store in a well ventilated place. Keep container tightly closed
Dispose of contents and container to an approved waste disposal plant

Other Non-GHS Classification:

WHMIS

NFPA/HMIS

NFPA SCALE (0-4)

HMIS RATINGS (0-4)

SECTION 3 : Composition/information on ingredients

Ingredients:

CAS 108-95-2	Phenol	>89 %
CAS 7732-18-5	Deionized Water	<11 %
CAS 6153-56-6	Oxalic acid, dihydrate	<0.01 %
		Percentages are by weight

SECTION 4 : First aid measures

Description of first aid measures

After inhalation: Move exposed to fresh air. Give artificial respiration if necessary. If breathing is difficult give oxygen.Loosen clothing and place exposed in a comfortable position.Seek medical assistance if cough or other symptoms appear.DO NOT use mouth - t o - mouth resuscitation if victim ingested or inhaled the substance.Induce artificial respiration with the aid of a pocket mask equipped with a one - way valve or other proper respiratory medical device.

After skin contact: Immediately enter emergency shower rinsing while removing contaminated clothing and shoes.Transport victim to the hospital.Wash hands and exposed skin with soap and plenty of water. Discard contaminated clothing in a manner which limits further exposure.SPEEDY ACTION IS CRITICAL!. Destroy contaminated shoes.

After eye contact: Incompatible materials.Continue rinsing eyes during transport to the hospital.Protect unexposed eye.Remove contact lenses while rinsing.DO NOT allow victim to rub eyes or keep eyes closed. Extensive irrigation with water is required for at least 30 minutes.

After swallowing: Rinse mouth with water.Do not induce vomiting. Never give anything by mouth to an unconscious person.Immediately seek medical attention.Notify a physician immediately and call Poison Control.

Most important symptoms and effects, both acute and delayed:

Irritation.Shortness of breath.Headache.Nausea.Dizziness.;Central Nervous System impairment. Upper Respiratory Tract irritation. Lung damage.Eye irritation. Skin irritation.

Indication of any immediate medical attention and special treatment needed:

If seeking medical attention provide SDS document to physician. Physician should treat symptomatically.

SECTION 5 : Firefighting measures

Extinguishing media

Suitable extinguishing agents: Use water, dry chemical, chemical foam, carbon dioxide, or alcohol-resistant foam.A vapor suppressing foam may be used to reduce vapors.

For safety reasons unsuitable extinguishing agents:

Special hazards arising from the substance or mixture:

Thermal decomposition can lead to release of irritating gases and vapors.

Advice for firefighters:

Protective equipment: Wear protective eyeware, gloves, and clothing. Refer to Section 8.

Additional information (precautions): Avoid dust formation.Avoid inhaling gases, fumes, dust, mist, vapor, and aerosols. Avoid contact with skin, eyes, and clothing.

SECTION 6 : Accidental release measures

Personal precautions, protective equipment and emergency procedures:

Ensure adequate ventilation.Ensure that air-handling systems are operational.Use spark proof tools.

Environmental precautions:

Should not be released into environment.Prevent from reaching drains, sewer, or waterway.

Methods and material for containment and cleaning up:

Wear protective eyeware, gloves, and clothing. Refer to Section 8.Always obey local regulations.If necessary use trained response staff or contractor. Evacuate personnel to safe areas. Containerize for disposal. Refer to Section 13.Keep in suitable closed containers for disposal.Absorb with suitable material and containerize for disposal .Remove all sources of ignition.

Reference to other sections:

SECTION 7 : Handling and storage

Precautions for safe handling:

Avoid contact with skin, eyes, and clothing.Follow good hygiene procedures when handling chemical materials. Refer to Section 8.Follow proper disposal methods. Refer to Section 13.Do not eat, drink, smoke, or use personal products when handling chemical substances.Keep away from heat, sparks and flame.Do not pressurize, cut, weld, braze, solder, drill, grind, or expose empty containers to heat, sparks or open flames

Conditions for safe storage, including any incompatibilities:

Store in a cool location.Store protected from moisture.Keep from contact with oxidizing materials.Keep away from food and beverages.Protect from freezing and physical damage.Provide ventilation for containers. Keep container tightly sealed. Store away from incompatible materials. Store protected from light. Keep container closed when not in use.

SECTION 8 : Exposure controls/personal protection




Control Parameters:

108-95-2, Phenol, TWA 5.000000 ppm USA. ACGIH
108-95-2 , Phenol, TWA 5.000000 ppm 19.000000 mg/m3 USA. NIOSH
108-95-2 , Phenol, TWA 5.000000 ppm 19.000000 mg/m3 USA. OSHA
108-95-2, Phenol, 250mg/g Creatinine Urine ACGIH (BEI)
6153-56-6, Oxalic acid dihydrate, TWA 1 mg/m3 USA. ACGIH
6153-56-6 , Oxalic acid dihydrate, TWA 1.000000 mg/m3 USA. OSHA
6153-56-6 , Oxalic acid dihydrate, TWA 1.000000 mg/m3 USA. NIOSH

Appropriate Engineering controls:

Emergency eye wash fountains and safety showers should be available in the immediate vicinity of use or handling. Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapor and mists below the applicable workplace exposure limits (Occupational Exposure Limits-OELs) indicated above.

Respiratory protection:

Not required under normal conditions of use. Where risk assessment shows air-purifying respirators are appropriate use a full-face particle respirator type N100 (US) or type P3 (EN 143) respirator cartridges as a backup to engineering controls.When necessary use NIOSH approved breathing equipment.

Protection of skin:

Select glove material impermeable and resistant to the substance.Select glove material based on rates of diffusion and degradation. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices.Use proper glove removal technique without touching outer surface. Avoid skin contact with used gloves.Wear protective clothing.

Phenol, Liquified

Eye protection: Tightly fitting safety goggles and faceshield (8 - inch minimum) are appropriate eye protection.Wear equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

General hygienic measures: Perform routine housekeeping.Wash hands before breaks and immediately after handling the product.Avoid contact with skin, eyes, and clothing.Before rewearing wash contaminated clothing. Discard contaminated shoes.

SECTION 9 : Physical and chemical properties

Appearance (physical state,color):	Clear colorless liquid	**Explosion limit lower**: **Explosion limit upper**:	1.7 %(V) 8.6 %(V)
Odor:	disinfectant odor	**Vapor pressure**:	3.2
Odor threshold:	Not Determined	**Vapor density**:	3.2
pH-value:	6.0	**Relative density**:	1.07 g/cm3
Melting/Freezing point:	42.8 °C	**Solubilities**:	Soluble in water
Boiling point/Boiling range:	182.0 °C	**Partition coefficient (n-octanol/water)**:	log Pow : 1.46
Flash point (closed cup):	79.4 °C	**Auto/Self-ignition temperature**:	715.0 °C
Evaporation rate:	Not Determined	**Decomposition temperature**:	Not Determined
Flammability (solid,gaseous):	Flammable	**Viscosity**:	a. Kinematic:Not Determined b. Dynamic: Not Determined
Density: Not Determined			

SECTION 10 : Stability and reactivity

Reactivity: Nonreactive under normal conditions.
Chemical stability: Stable under normal conditions.
Possible hazardous reactions: None under normal processing.
Conditions to avoid: Incompatible materials.Light, ignition sources, excess heat, exposure to moist air or water.
Incompatible materials: Strong oxidizing agents, isocyanates, acetaldehyde, calcium hypochlorite, peroxomonosulfuric acid, nitrobenzene, sodium nitrite, aluminum chloride, peroxydisulfuric acid, 1,3 - butadiene, boron trifluoride diethyl ether.
Hazardous decomposition products: Carbon oxides.

SECTION 11 : Toxicological information

Acute Toxicity:		
Oral:	108-95-2	LD50 Oral - Rat - 317.0 mg/kg (Behavioral:Convulsions or effect on seizure threshold)
Inhalation:	108-95-2	LC50 Inhalation - Rat - 8 h - 900 mg/m3

Oral:	108-95-2	LD50 Dermal - Rabbit - 630.0 mg/kg
Oral:	6153-56-6	LD50 Oral - Rat - 1,080 mg/kg
Chronic Toxicity: No additional information.		
Corrosion Irritation:		
Dermal:	108-95-2	Skin - Rabbit Result : Severe skin irritation - 24 h
Ocular:	108-95-2	Eyes - Rabbit Result : Corrosive to eyes
Dermal:	6153-56-6	Skin - Rabbit Result : Mild skin irritation
Ocular:	6153-56-6	Eyes - Rabbit Result : Risk of serious damage to eyes.
Sensitization:		No additional information.
Single Target Organ (STOT):		108-95-2: May cause damage to organs through prolonged or repeated exposure
Numerical Measures:		No additional information.
Carcinogenicity:		No additional information.
Mutagenicity:		No additional information.
Reproductive Toxicity:		6153-56-6: P ossible risk of congenital malformation in the fetus.

SECTION 12 : Ecological information

Ecotoxicity

108-95-2: LC50 - Leuciscus idus (Golden orfe) - 14.00 - 25.00 mg/l - 48 h

108-95-2: LC50 - Carassius auratus (goldfish) - 36.10 - 68.80 mg/l - 96 h

108-95-2: EC50 - Daphnia magna (Water flea) - 56 mg/l - 48 h

108-95-2: EC50 - Chlorella vulgaris (Fresh water algae) - 370.00 mg/l - 96 h

6153-56-6: LC50 - Leuciscus idus (Golden orfe) - 160 mg/l - 48 h

6153-56-6: EC50 - Daphnia magna (Water flea) - 137 mg/l - 48 h

Persistence and degradability: 108-95-2: Result : - Readily biodegradable. Phenol, Liquified: Half - life: day 15 hours, night 12 minutes
Bioaccumulative potential:
Mobility in soil: Mobile in soil and water.
Other adverse effects:

SECTION 13 : Disposal considerations

Waste disposal recommendations:

Dissolve or mix the material with a combustible solvent and burn in a chemical incinerator equipped with an afterburner and scrubber.Contact a licensed professional waste disposal service to dispose of this material.Dispose of empty containers as unused product.Product or containers must not be disposed together with household garbage. It is the responsibility of the waste generator to properly characterize all waste materials according to applicable regulatory entities (US 40CFR262.11). Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations. Ensure complete and accurate classification.

SECTION 14 : Transport information

UN-Number
UN2821

UN proper shipping name
Phenol Solutions

Transport hazard class(es)

Class:
6.1 Toxic substances

Packing group:II
Environmental hazard:
Transport in bulk:
Special precautions for user:

SECTION 15 : Regulatory information

United States (USA)

SARA Section 311/312 (Specific toxic chemical listings):
Acute, Chronic, Fire

SARA Section 313 (Specific toxic chemical listings):
108-95-2 Phenol

RCRA (hazardous waste code):
None of the ingredients is listed

TSCA (Toxic Substances Control Act):
All ingredients are listed.

CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act):
108-95-2 Phenol 1000 lb

Proposition 65 (California):

Chemicals known to cause cancer:
None of the ingredients is listed

Chemicals known to cause reproductive toxicity for females:
None of the ingredients is listed

Chemicals known to cause reproductive toxicity for males:
None of the ingredients is listed

Chemicals known to cause developmental toxicity:
None of the ingredients is listed

Canada

Canadian Domestic Substances List (DSL):
All ingredients are listed.

Canadian NPRI Ingredient Disclosure list (limit 0.1%):

None of the ingredients is listed

Canadian NPRI Ingredient Disclosure list (limit 1%):

108-95-2 Phenol

SECTION 16 : Other information

This product has been classified in accordance with hazard criteria of the Controlled Products Regulations and the SDS contains all the information required by the Controlled Products Regulations. Note: . The responsibility to provide a safe workplace remains with the user. The user should consider the health hazards and safety information contained herein as a guide and should take those precautions required in an individual operation to instruct employees and develop work practice procedures for a safe work environment.The information contained herein is, to the best of our knowledge and belief, accurate. However, since the conditions of handling and use are beyond our control, we make no guarantee of results, and assume no liability for damages incurred by the use of this material. It is the responsibility of the user to comply with all applicable laws and regulations applicable to this material.

GHS Full Text Phrases:

Abbreviations and acronyms:

Effective date : 03.03.2015
Last updated : 03.19.2015

➢ UV-Vis spectroscopy or spectrophotometer

Ultraviolet-Visible spectroscopy is an analytical techniques used to measure the concentration of a sample. A beam with wavelength between 180-1100 nm passes through the cuvette, the sample absorbs this UV or visible radiation. It was in this project to determine the concentration of phenol and to create a calibration curve.

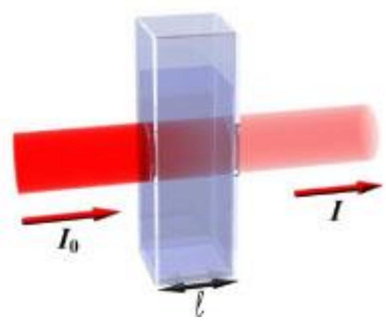


Figure A 1: Light beam passes through the cuvette.

Figure A 2: UV-Vis Spectrophotometer.

Figure A 3: Liquid phenol used in this study.

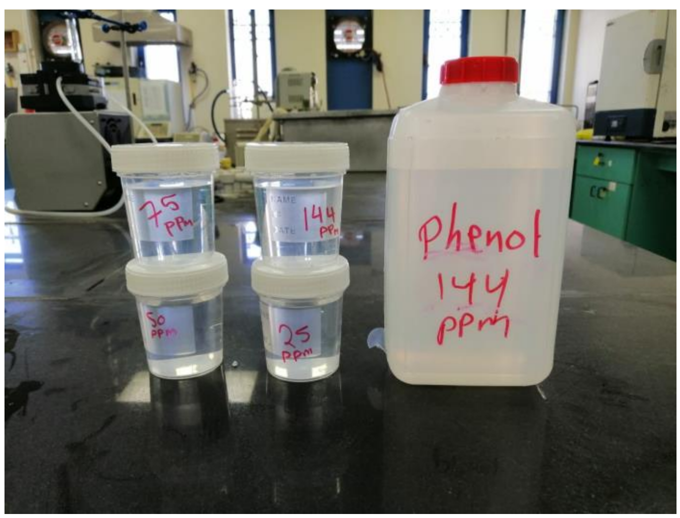


Figure A 4: Stock and diluted solutions of phenol with 100, 75, 50 and 25 mg/L.

Figure A 5: Glass and lab tools used in the experiment.

Spectrum Peak Pick Report

22/10/2019 12:35:04 a

Data Set: File_191022_123256.spc - RawData

No.	P/V	Wavelength	Abs.	Description
1	⊕	339.60	0.002	
2	⊕	269.60	1.164	
3	⊕	206.20	3.325	
4	O	344.00	-0.000	
5	O	238.80	0.097	
6	O	203.40	3.172	

[Measurement Properties]
Wavelength Range (nm.): 200.00 to 400.00
Scan Speed: Fast
Sampling Interval: 0.2
Auto Sampling Interval: Enabled
Scan Mode: Single

[Instrument Properties]
Instrument Type: UV-1800 Series
Measuring Mode: Absorbance
Slit Width: 1.0 nm
Light Source Change Wavelength: 340.0 nm
S/R Exchange: Normal

[Attachment Properties]
Attachment: None

[Operation]
Threshold: 0.0010000
Points: 4
InterPolate: Disabled
Average: Disabled

[Sample Preparation Properties]
Weight:
Volume:
Dilution:
Path Length:
Additional Information:

Page 1 / 1

Figure A 6: Spectrum peak of phenol.

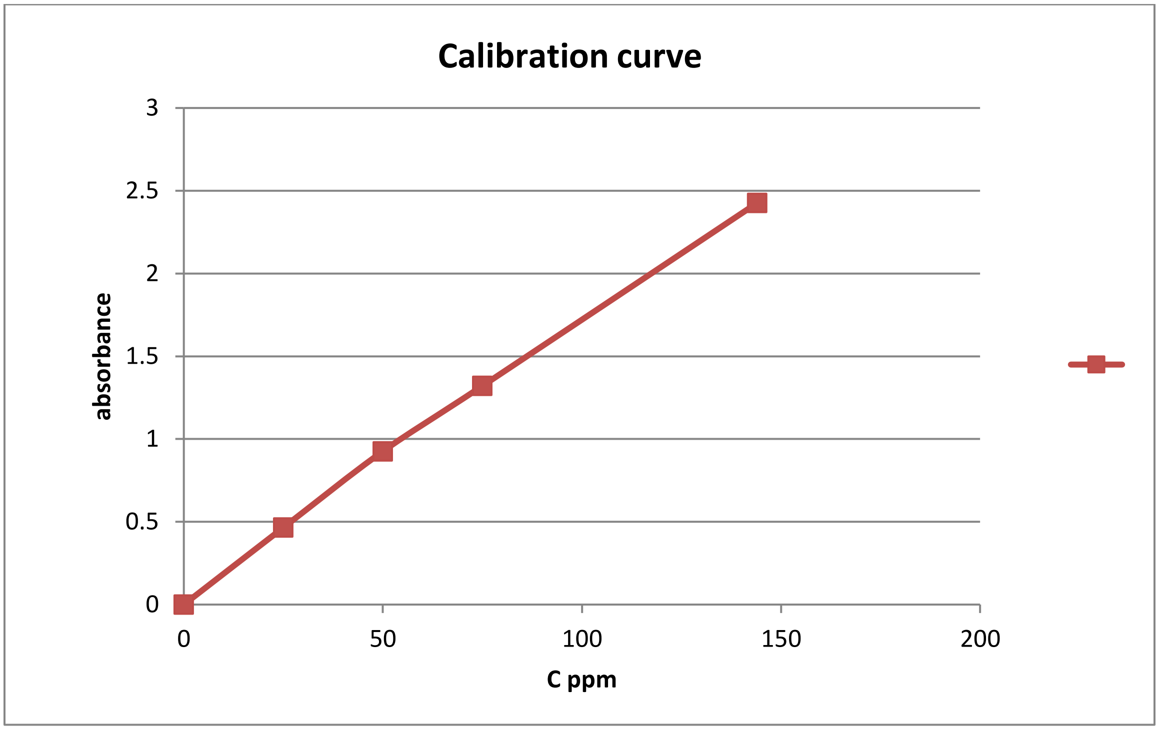


Figure A 7: Calibration curve.

- **ADSIM procedure:**

The following steps show the Aspen procedure that was considered for simulation in this project:

8. The program was opened; the components were inserted to the component list as shown in **Figure A 8**, where Aspen property system was used for the physical property configuration.

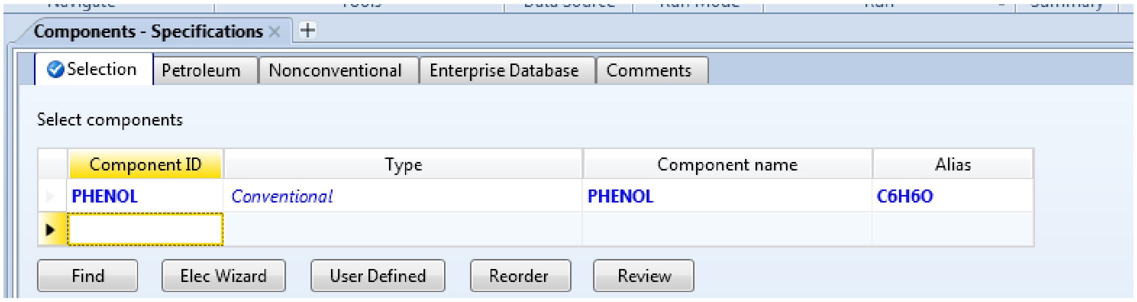


Figure A 8: Aspen components list.

9. The appropriate property method was specified, PENG-ROB as shown in **Figure A 9** below.

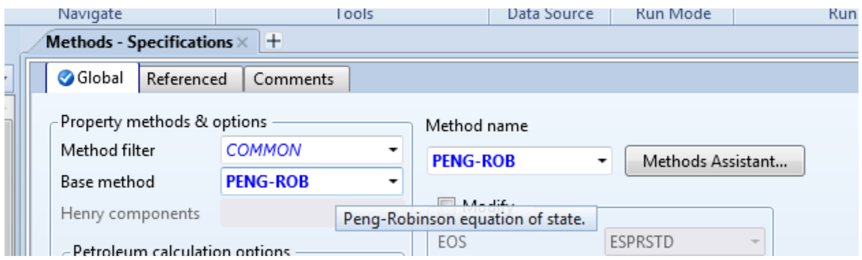


Figure A 9: Aspen property method.

10. After that, the system was run, and the property document was saved as PropsPlus.aprbkp**.** The green square, which was shown in **Figure A** 10, means that the properties are successfully configured in the properties configuration form.

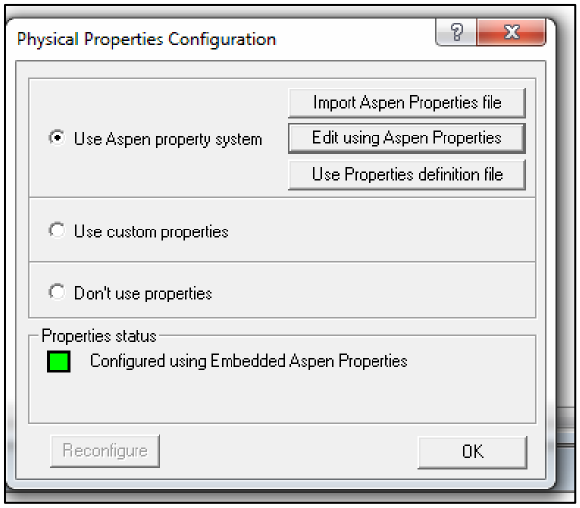


Figure A 10: Physical properties configuration.

11. The process was created as shown in **Figure A** 11 by adding the liquid feed, liquid bed and liquid product from (library-ADSIM) to the flowsheet and connected to each other using the connection.

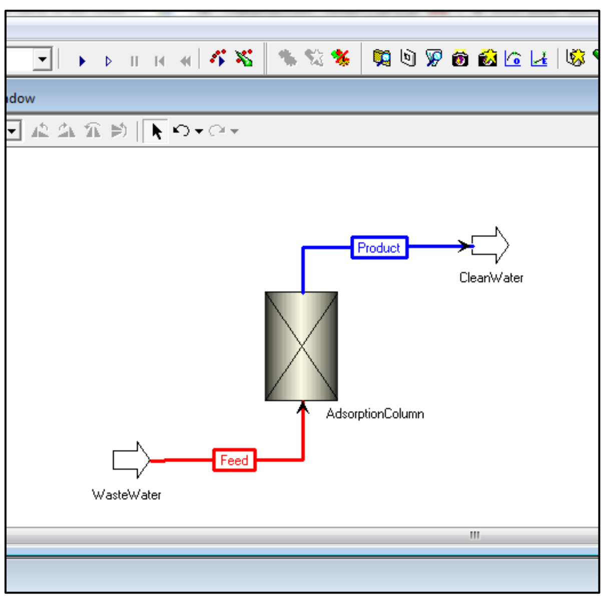
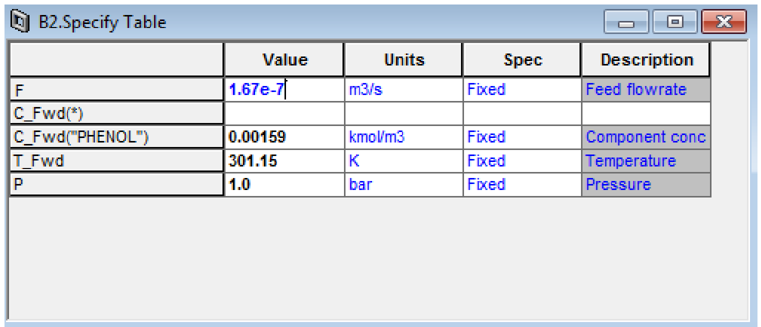


Figure A 11: Adsorption process flowsheet.

12. Operating parameters; flow rate, concentration, temperature and pressure were inserted for the feed stream by double click on the liquid feed. The same for the liquid product. **Figure A 12** shows the liquid feed configuration

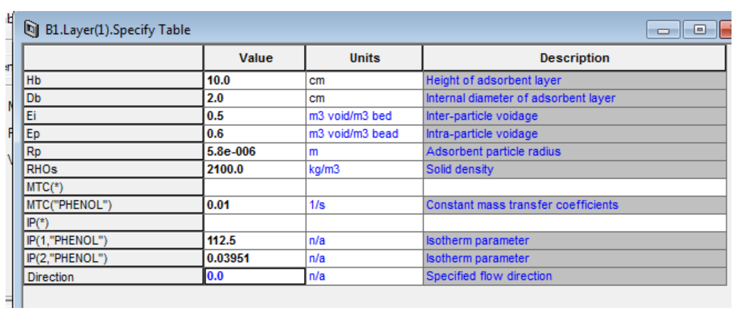


B2.Specify Table

	Value	Units	Spec	Description
F	1.67e-7	m3/s	Fixed	Feed flowrate
C_Fwd(*)				
C_Fwd("PHENOL")	0.00159	kmol/m3	Fixed	Component conc
T_Fwd	301.15	K	Fixed	Temperature
P	1.0	bar	Fixed	Pressure

Figure A 12: Liquid feed (wastewater) configurations.

13. The configurations of the bed were added by double click on the liquid bed as shown in **Figure A 13**.



B1.Layer(1).Specify Table

	Value	Units	Description
Hb	10.0	cm	Height of adsorbent layer
Db	2.0	cm	Internal diameter of adsorbent layer
Ei	0.5	m3 void/m3 bed	Inter-particle voidage
Ep	0.6	m3 void/m3 bead	Intra-particle voidage
Rp	5.8e-006	m	Adsorbent particle radius
RHOs	2100.0	kg/m3	Solid density
MTC(*)			
MTC("PHENOL")	0.01	1/s	Constant mass transfer coefficients
IP(*)			
IP(1,"PHENOL")	112.5	n/a	Isotherm parameter
IP(2,"PHENOL")	0.03951	n/a	Isotherm parameter
Direction	0.0	n/a	Specified flow direction

Figure A 13: Liquid bed configuration.

14. The simulation was run to get the breakthrough curve as shown in **Figure A 14**.

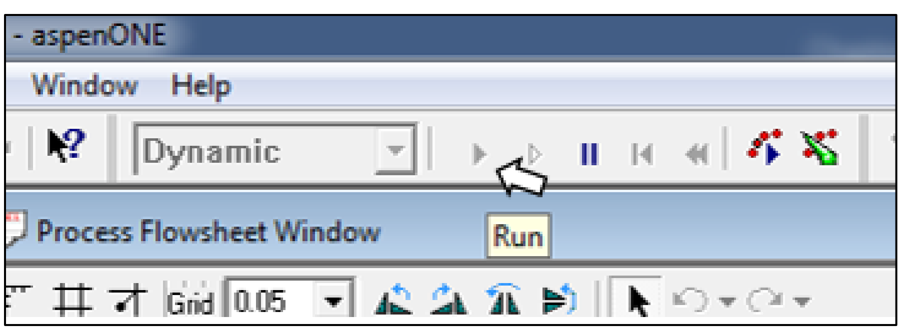


Figure A 14: Simulation run.

- **MTC estimation:**

Mass transfer coefficient (MTC):

The MTC was calculated by aspen, by following the steps below.

3. 0.01 (1/min) was inserted to liquid bed configuration in ADSIM as an initial guess for MTC value (**Figure A15**).

	Value	Units	Description
Hb	10.0	cm	Height of adsorbent layer
Db	2.0	cm	Internal diameter of adsorbent layer
Ei	0.5	m3 void/m3 bed	Inter-particle voidage
Ep	0.6	m3 void/m3 bead	Intra-particle voidage
Rp	5.8e-006	m	Adsorbent particle radius
RHOs	2100.0	kg/m3	Solid density
MTC(*)			
MTC("PHENOL")	0.01	1/min	Constant mass transfer coefficients
IP(*)			
IP(1,"PHENOL")	112.5	n/a	Isotherm parameter
IP(2,"PHENOL")	0.03951	n/a	Isotherm parameter
Direction	0.0	n/a	Specified flow direction

Figure A15 : Initial guess for MTC value.

4. The concentration of phenol at several times (**Table A 1**) was calculated from experimental breakthrough curves (**Figure A 16**).

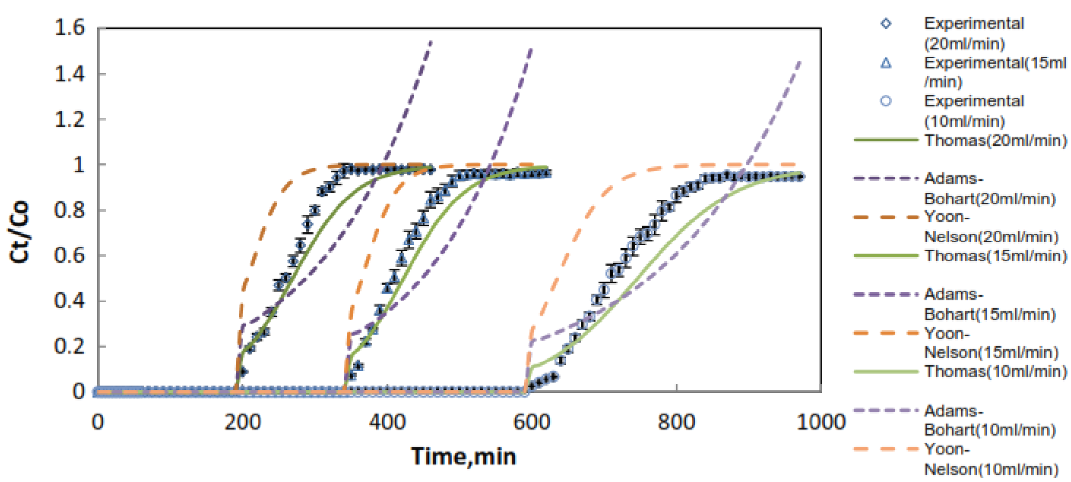


Figure A 16: Experimental breakthrough curve at 150mg/l concentration and 10 cm bed height.

Table A 1: The required data for MTC calculations.

C_0 (mg/l)	150	
C_0 (mol/l)	$1.594e^{-6}$	
Q(ml/min)	20	
time	**C/C0**	**C**
200	0	0
250	0.35	0.000558
300	0.8	0.001275
350	0.95	0.001514
400	1	0.001594

The next steps were available at the following links:

https://www.youtube.com/watch?v=Pr5CyXpdgxY

https://www.youtube.com/watch?v=KmH7XGtkhTM.

Appendix B

- Calibration curve:

Sample of calculation:

Required mass = 0.16 g.

Volume of solution = 1000 ml.

Purity of phenol liquid = 90%.

$$Conc\ of\ the\ stock\ soln\,\frac{mg}{L} = \frac{mass\ of\ liquid\ phenol\ mg}{Volumeof\ soln\ L} \times Purity$$

$$Conc\ of\ the\ stock\ soln\,\frac{mg}{L} = \frac{0.16\ g}{1000\ ml} \times \frac{1000\ mg}{1\ g} \times \frac{1000\ ml}{1\ L} \times 0.9$$

$Conc\ of\ the\ stock\ soln = 144\frac{mg}{L} = 144\ ppm.$

$$144\ \frac{mg}{L} \times \frac{1\ mol}{94.11\ g} \times \frac{1\ L}{1000\ ml} = 1.53 \times 10^{-6}\frac{mol}{ml}$$

To prepare a solution with 75 ppm, the required volume that will withdraw from the stock was calculated by the following equation:

$$(Conc \times Volume_{Required})_{Stock} = (Conc \times Volume)_{Dilute}$$

$$75\ \frac{mg}{L} \times \frac{1\ mol}{94.11\ g} \times \frac{1\ L}{1000\ ml} = 7.97 \times 10^{-7}\frac{mol}{ml}$$

$$(1.53 \times 10^{-6}\frac{mol}{ml} \times Volume)_{Stock} = (7.97 \times 10^{-7}\frac{mol}{ml} \times 100\ ml)_{Dilute}$$

$$Volume\ that\ will\ withdraw\ from\ the\ stock = 52.0833\ ml$$

To prepare a solution with 50 and 25 ppm, the required volume that will withdraw from the stock was calculated by the same calculation.

$$Volume\ that\ will\ withdraw\ from\ the\ stock\ tp\ prepare\ a\ solution\ with\ 50\ ppm = 34.722\ ml$$

$$Volume\ that\ will\ withdraw\ from\ the\ stock\ tp\ prepare\ a\ solution\ with\ 25\ ppm = 17.361\ ml$$