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Characterization and Application of Activated Carbon from Oil Palm Shell Prepared By Physical Activation and Nitric Acid for the Removal of Phenol and 2-Chlorophenol

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Abstract: ***Activated carbon from oil palm shell was prepared by physical activation and washing with nitric acid solution. The textural properties of activated carbon were obtained: BET surface area 491.16m^2/g, Langmuir surface area 723.55m^2/g, micropore volume 0.27cc/g and pore radius 7.10 Å. The activated carbon was evaluated as an adsorbent for the removal of phenol and 2cholorophenol from aqueous solution with batch adsorption process. Equilibrium pH values showed the maximum adsorption capacity was obtained at pH 5 and 7 for phenol and 2-chlorophenol, respectively. The equilibrium adsorption of weight activated carbon was evaluated with Langmuir and Freundlich isotherm model conducting of removal of phenol and 2-chlorophenol. The result indicates that both Langmuir and Freundlich isotherm models are favorable for phenol adsorption process with0.944 and 0.996, respectively. However, 2-chlorophenol is only favorable for Freundlich isotherm model with correlation coefficient (R^2)0.981.***

Keywords: Activated carbon, Nitric acid, Phenol, 2-Chlorophenol,Langmuir and Freundlich

1. Introduction

Phenolic derivatives such as phenols and 2-chlorophenol are widely used in the industrial chemicalas intermediates in the synthesis of resin, plastic, adhesive, pesticides, and insecticides, in pulp bleaching and among others. It is also found as a disinfectant in household cleaners, in mouthwash and in cigarettes[1, 2]. Recently, the presence of these chemicals increase in drinking water, municipal and industrial waste, represent a serious problem in the environment, human health and aquatic life. These chemical are carcinogenic and harmful toxic. In low concentration of this chemical can cause unpleasant taste, odor to water bodies and having negative effect in the biological process. In the last few years, a great attention had been focused on the detection of phenol derivatives due to their ability to danger for human health. The adsorption of phenol and 2-chlorophenol from solution has been investigated in different adsorbents. One of the alternative process for waste water treatment is the adsorption technique using activated carbon as an adsorbent[3].

Activated carbon is well-known adsorbent due to its excellent and versatile characteristics that allow contaminant such as gas or liquid into internal pore surface and high degree of surface chemical bonding. The effectiveness of activated carbon is related to the pore structure: surface, pore size distribution, pore volume and surface chemistry which have relationship with the capacity adsorption. Activated carbon with the highly-predominant proportion of micro-porous structures it was applicable used in various applications such as adsorbent for purification and separation of pollutants in liquid or gas, catalyst and catalyst support.

Activated carbon can be prepared from low cost material with high carbonaceous compound such as coconut shell, bamboo, palm oil shell, bagasse among others. Various techniques were conducted to prepare activated carbon including physical and chemical processes[4]. Improving adsorption capacity of activated carbon also can be enhanced by creating surface functional groups. For example, impregnating of ammonia into activated carbon at elevated temperature has been investigated to modify the surface functional group and porous texture. Treatment process with chemical impregnation has to be optimized to favor the formation of specific of N or O containing surface functional group such as carboxylic, lactone, phenol, carbonyl, pyrone, chromene, quinone, and ether groups[5, 6].

In this paper, activated carbon was prepared by physical activation under nitrogen and directly continued under carbon dioxide gas at 800°C. The activated carbon was introducing with ammonia in order to clean and create the surface functional group on the surface of activated carbon. In addition, it could improve its capacity properties. Application of this adsorbent was conducted to the removal of phenol and 2chlorofenol from aqueous solution. Textural characteristics of activated carbon were carried out by Quantachrome pore size analyzer, NOVA 2200e, FTIR and UV-Visible.

2. Experimental

2.1 Materials and Methods

Phenol, 2-chlorophenol, nitric acid, sodium hydroxide, potassium bromide were used as received without purification. The spectra of the functional group were recorded with Fourier Transform Infrared Spectroscopy (FTIR) Shimadzu. Porous structure of activated carbon was determined with Quantachrome Nova 2200e. Phenol and 2-chlorophenol was evaluated by UV-Vis Hitachi U 2900. Oil palm shell as raw material was obtained at open area around palm oil industry.

2.2 Preparation of activated carbon

Oil palm shell waste is biomass collected at open area around palm oil industry. Sample was washed with distilled water to remove dirt and oil attached on the surface of shell and dried in the oven for 24 hours at 120ºC. Dried sample was crushed and sieve into granular size of 0.1-0.5 mm. sample was placed into reactor and followed into graphite furnace. Carbonization process was started from room temperature to 800ºC and kept at 800ºC for 2.5 hours as a contact time. During carbonization process, nitrogen gas was passed through into reactor with flow rate 250 cc/min. Thereafter, the gas nitrogen was directly changed with carbon dioxide gas for another 2 hours.

After cooling down to room temperature, the activated carbon was impregnated into 10 M of HNO_3 and refluxed at 80-85ºCfor 5 hours. The activated carbon was filtered and washed with hot distilled water to pH 6-7 by dropping 1.0 N of NaOH. The neutral activated carbon was carbonized into graphite furnace at 150ºC for 2 hours.

2.3 Nitrogen adsorption desorption isotherm.

A small amount of activated carbon was put into the tube of Quanta-chrome for degassing process carried out at 350ºC for 8 hours. Thereafter, the effectiveness of activated carbon was analyzed using nitrogen adsorption isotherm at 77K. The data of nitrogen adsorption-desorption isotherm was used to evaluate the pore structure involving surface area, pore volume and pore size distribution. Characterization of surface area was calculated by BET and Langmuir methods, micropore volume and pore size distribution were evaluated by Dubinin Redushkevich (DR) and Dubinin Astakov, respectively.

2.4 Functional group of activated carbon.

Determination of surface functional group was conducted by FTIR at range of wave length 4000-400 cm^{-1} using pellet KBr.

2.5 Adsorption of phenol and 2-chlorophenol

In order to evaluate the significant adsorption of phenol and 2-chlorophenol using activated carbon was carried out with batch method using various variables involving pH, contact times and different mass. Determination of phenol and 2-chlorophenol were analyzed by UV-Vis spectrophotometer at wavelength of 270 and 274 nm for Phenol and 2-2-chlorophenol, respectively. The evaluation of adsorption capacity was estimated with the following equation:

$$qt = \frac{(Co - Ct)V}{W}$$

The *Co* and *Ct* are the initial concentration and equilibrium state (mg/L), respectively. *Qe* (m/L) is the equilibrium amount *q* adsorbed per unit mass of adsorbent. The *V* is volume of the solution and *W* (m/gr) is the mass of adsorbent

3. Results and Discussion

3.1 Nitrogen isotherm of activated carbon

During the physisorption process, the experiment was set up with relative pressure in range of 0.01-0.99 for purified nitrogen gas. Figure 1 shows data of nitrogen adsorption-desorption isotherm for activated carbon which was obtained at 77K. The plot of nitrogen adsorption-desorption isotherm sharply increased at low relative pressure (P/Po= 0.00–0.40) and plateau at higher relative pressure (P/Po=0.40-≈1.00). Based on the IUPAC classification at low relative pressure, the isotherm plot exhibits Type I isotherm model which is relationship with the formation of monolayer adsorption. This model exhibited a predominantly microporous structure[7]. However, the nitrogen isotherm plot at higher relative pressure (P/Po= 0.40-0.80) show a small hysteresis loop exhibiting Type IV isotherm. This model is generally associated with capillary condensation of mesoporous structure containing a small amount of mesopore [8, 9].On the contrary, it supposes that activated carbon exhibits predominantly homogeneous micropores with a very small mesopore,

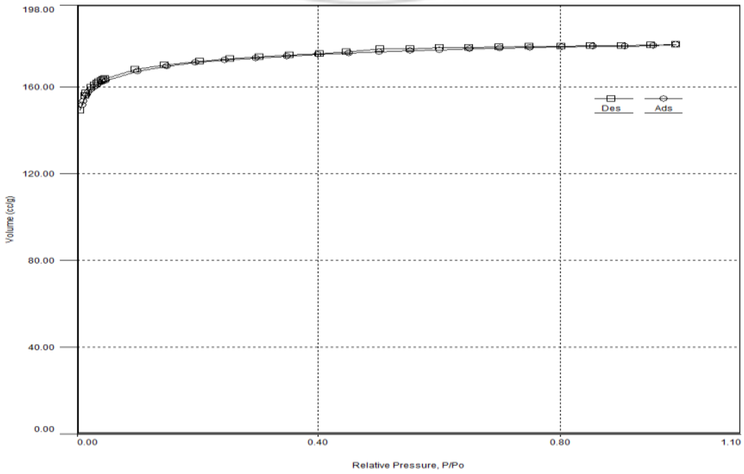

Figure 1: Nitrogen adsorption-desorption isotherm of activated carbon

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Figure 2 shows the pore size distribution of activated carbon which was estimated by the Dubinin Astakhov (D-A) method. The result shows that pore diameter are presence at around 4 -16 Å. These sizes indicate that the activated carbons have microporous structure with pore diameter less than 20 Å. Based on the equation, the D-A method required characteristic energy (*Eo*) and *n* parameter distributions[10]. In this approach, *n* is an exponent relating with the width of the distribution plot of adsorption energy, which is related to the pore size distribution. Values of *n* between 1 and 3 have been obtained for large carbon adsorbents. Values of $n \geq 3$ represents the homogeneously narrow micropores of molecular sieve carbons while values $n \leq 2$ show heterogeneous micropores with wider pore size distribution. The value of *n* is 1.9 shown in Table 1.

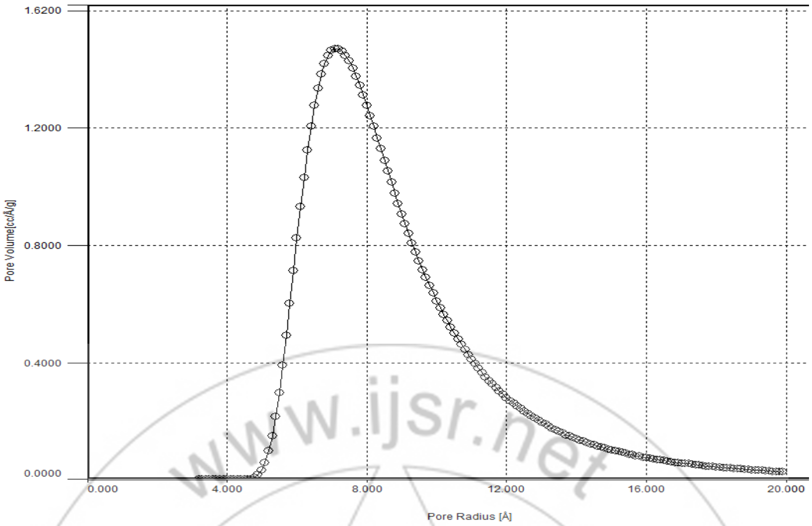

Figure 2: D-A plot micropore distribution of activated carbon

3.2 Surface Areas of Activated carbon

Figure 3 shows the plot of activated carbon having linier regression at relative pressure less than 0.45which is widely used to determination best-fitting isotherm. The values of the Langmuir plot shows Slope = 4.813, Intercept 0.0051 and Correlation coefficient, r = 1.00. These values indicate that there is a strong positive evidence to calculate the surface area of activated carbon following the Langmuir method (Fig.3A).Other properties with microporous structures can be estimated by the Dubinin Radushkevich and the Dubinin Astakhov for micropores volume and pore radius, respectively. Liner regression of activated carbon using BET plot (Fig. 3B) shows an error in the best-fitting isotherm with correlation coefficient (r) less than 1.00 (the perfect, r=1.00)[11].However, the estimation of surface area using BET method might also support the data of porous structure. The BET surface area was carried out at relative pressure in the range of 0.05-0.35. It assumed that that the pore could be narrow mesoporous structures. Determination of micropores surface area and pore diameter were calculated by t-plot and BHJ methods, respectively. Total pore volume of the activated carbon was obtained at maximum relative pressure, 0.99. The Textural properties of surface area for activated carbon were shown in Table 1.

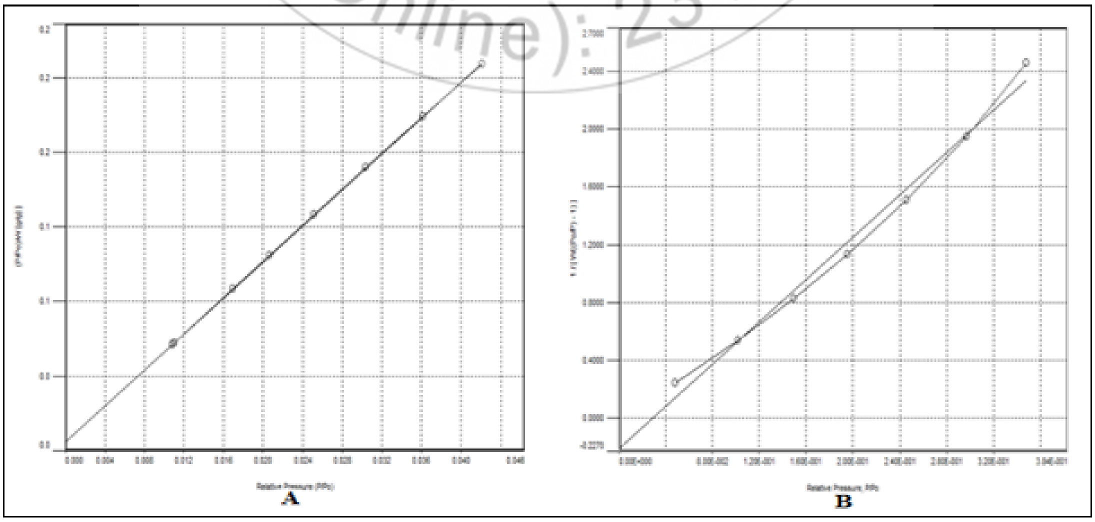

Figure 3: Langmuir adsorption (A) and BET adsorption plot of activated carbon

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Table 1: Textural properties of activated carbon

Langmuir method		*BET method*	
Langmuir surface area	723.55 m^2/g	Multipoint bet surface area	491.16 m^2/g
DR method micropore volume	0.27 cc/g	t-plot method micropore volume	0.25 cc/g
DR method micropore surface area	746.08 m^2/g	t-plot method micropore surface area	463.5 m^2/g
		External surface area	27.7 m^2/g
DA method pore radius, n=1.9	7.10 Å	BJH method pore radius	17.06 Å
		Total pore volume (P/Po=0.99)	0.28 cc/g

Dubinin-Radushkevich (DR), Dubinin Astakhov (DA)

3.2 Functional groups of activated carbon

Investigation of the functional group attached on the surface of activated carbon was carried out by FTIR. Fig. 4 shows the result of FTIR spectra of functional group modified with nitric acid solution. A broad spectrum at band 3460 cm^{-1} was assigned as O-H stretching vibration of hydroxyl group as a result of modification. A band at 1636 $cm^{-1}$is generally attributed toC=O stretching vibration in carbonyl group, and it is also associated to C=C stretching vibration in aromatic rings. A weak band at1384 cm^{-1} is attributed to C-N stretching vibration to amines group. A medium band 1086cm^{-1} is ascribed to C–O stretching vibration in ether groups and C-N stretching vibration in amine groups. The presence of band at 669 cm^{-1} is ascribed to C-H in out-of-plane bending in the edges of aromatic rings.

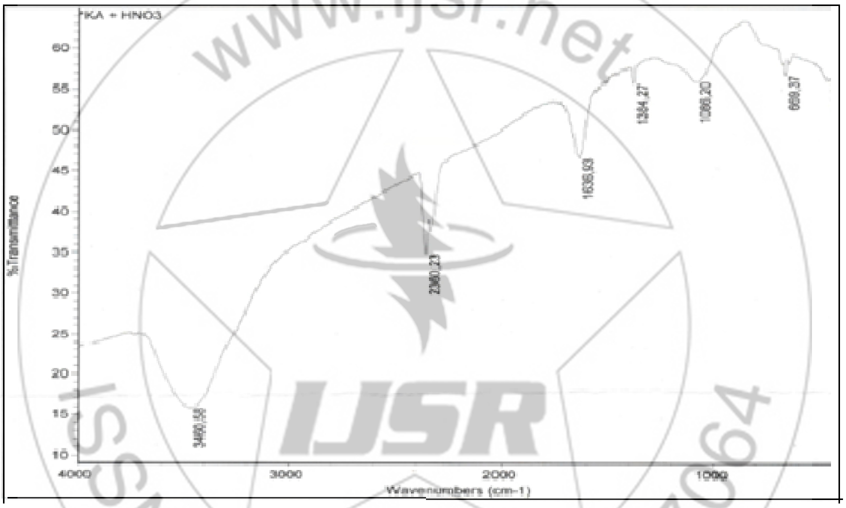

Figure 4: The FTIR spectra of activated carbon after modified with nitric acid

3.3 Applications of Activated Carbon for Adsorption of phenol and 2-chlorophenol

3.3.1. Effect of contact time on the adsorption process

The effects of adsorption capacity were set up at variety of contact times to find the optimum time of adsorption process [12].Fig 5 (a) and (b)show the adsorption capacity of phenol and 2-chlorophenol on activated carbon, respectively. In general, the adsorption capacity of activated carbon increased with increasing contact times. Large amount of phenol and 2-chlorophenol were adsorbed and reached a maximum adsorption at 45 minutes. Adsorption capacity sharply decreases after reaching equilibrium process. This phenomenon was assumed that the adsorption capacity was related to the formation of pore size of pore structure which has wide microporous to narrow mesoporous structures.

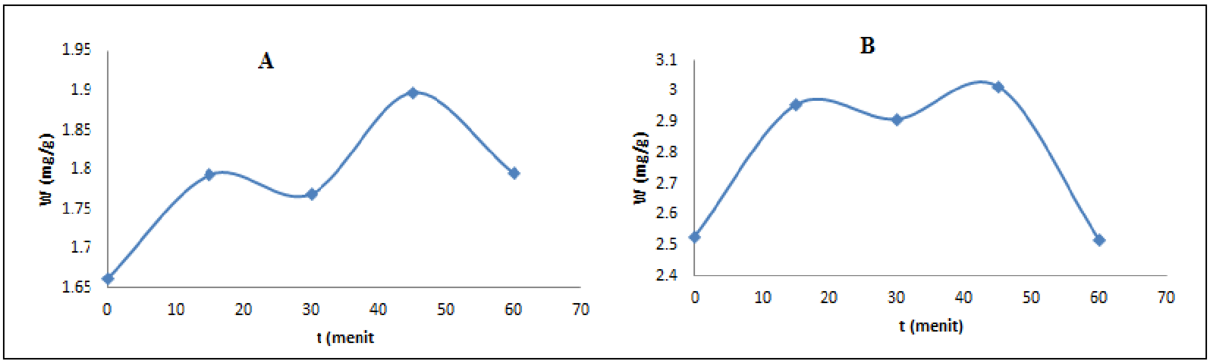

Figure 5: Effect of contact times on the adsorption capacity of phenol (A)and 2-chlorophenol (B) on the activated carbon

3.3.2. Effect of pH on the adsorption on process

The pH is an important factor to study the adsorption capacity activated carbon. The effect of pH on the adsorption capacity was shown on Fig. 6. Large adsorption capacities were shown at pH 5 for phenol and pH 7 for 2-chlorophenol. It assumed that the adsorption process of phenol and 2-chlorophenol using activated carbon involved both processes physisorption and chemisorption[13].

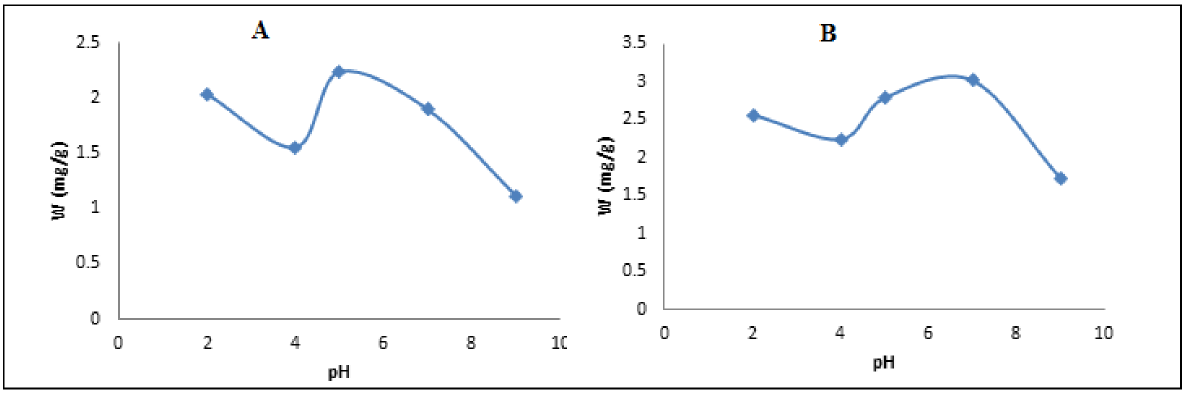

Figure 6: Effect of pH on the adsorption capacity of phenol (A) and 2-chlorophenol (B) on the activated carbon

It was mentioned at previous research, the absorption of aromatic compounds including phenol and 2-chlorophenol could not completely describe the mechanism process by which the process took place. Two type mechanisms of phenol have been reported from previous work. One involves interaction between carbonyl functional group as an electron donor of surface activated carbon and aromatic ring as an acceptor functional group of phenol. Second mechanism involves the interaction between basic site of activated carbon as an electron donor and aromatic ring as an electron donor of phenol. [14].The adsorption process of activated carbon involves chemisorption possessing basic or acid properties and, or both properties as an amphoteric properties. These properties show positively or negatively charged characters on the surface which is depended on pH solution. The Activated carbon with more negatively charged on the surface is obtained at higher pH value and this favorable to bond of cationic group resulting the decreasing of electrostatic interaction between phenol and 2cholorophenol and the surface of activated carbon [15]. This phenomenon assumed that increasing the carbonyl functional group (more oxygen functional group) on the activated carbon increase the strength of donor acceptor interaction. In other words, it is acceptable data that increase the carbonyl and basic functional group could influence of adsorptive capacity of phenol.

3.3.4. Adsorption Isotherm

Adsorption isotherm describes the relationship between the amount of phenol and 2-chlorophenol adsorbed on activated carbon and concentration dissolved adsorbate in the solution equilibrium. Fig. 7 shows the plot adsorption of phenol and 2-chlorophenol with the used of activated carbon modified nitric acid. The result indicated that the amount of phenol and 2-chlorophenol adsorbed increase with an increasing concentration.

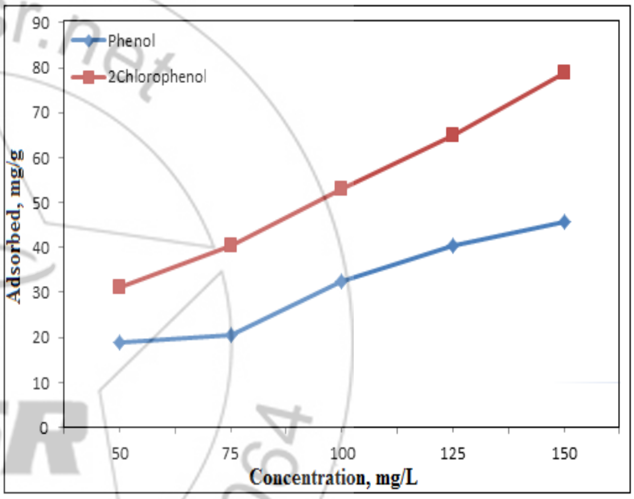

Figure 7: The plot adsorption of phenol and 2-chlorophenol using activated carbon

In this study, the equilibrium adsorption of phenol and 2-chlorophenol were evaluated using Langmuir and Freundlichisotherm model. Adsorption with Langmuir isotherm model is related to the monolayer adsorption indicating the presence of microporous structures of activated carbon. The Langmuir equation is expressed as follows.

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}$$

Where: C_e is the equilibrium concentration (mg/l), $q_e$is amount adsorbed at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g), K_L is the equilibrium adsorption constant related to the free energy of the adsorption (L/mg). A plot of C_e/q_e against C_e results linier line, while q_m and k_L are obtained from the intercept and slope [16, 17].

The Freundlich isotherm model follows the equation below.

$$\log (q_e) = \log K_F + 1/n(\log C_e)$$

Where qe is the adsorption intensity (L/mg), K_F and n show Freundlich constant, C_e is the concentration of adsorbate (phenol and 2-chlorophenol) at equilibrium (g/L). If the plot of q_e versus log C_e results a liner line, and then the sorption process follows a Freundlichisotherm model. The K_F and 1/n can be obtained from the intercept and slope of the straight line. The plot of Langmuir and Freundlich isotherm models of phenol and 2-chlorophenol shows straight line posted in Fig 8 and 9.

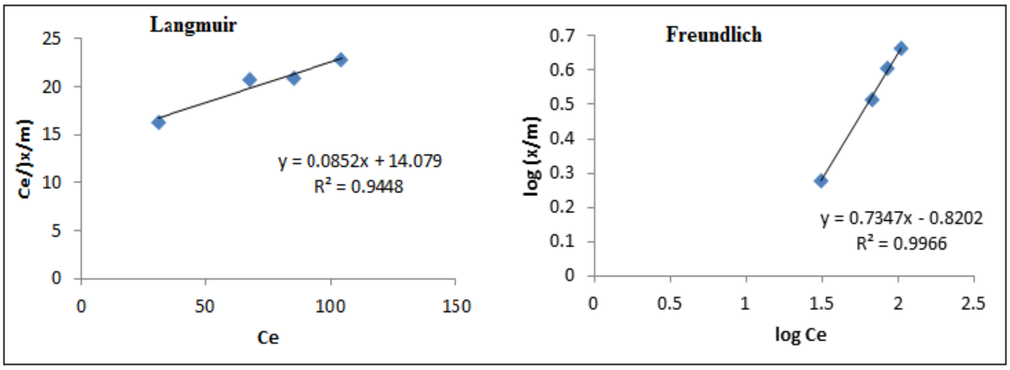

Figure 8: Plot of adsorption isotherm model of phenol

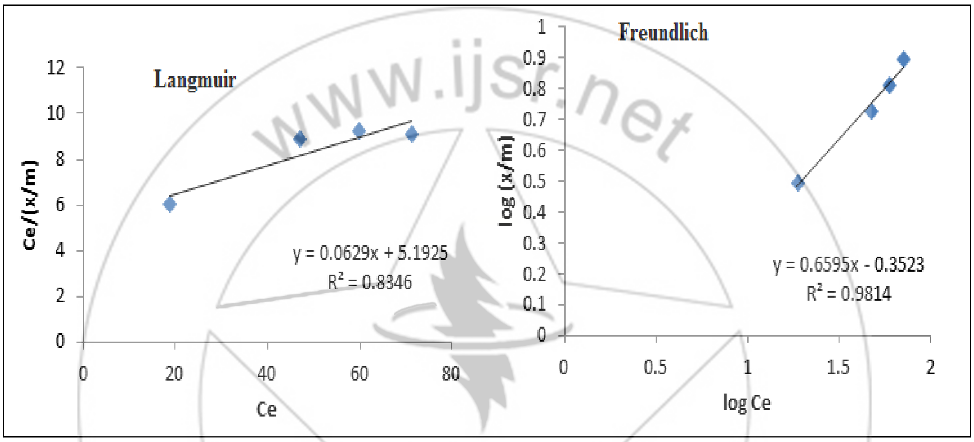

Figure 9: Plot of adsorption isotherm model of 2-chlorophenol

Table 2: Langmuir and Freundlich model for the adsorption of phenol and 2-cholorphenol

Type of Adsorbate	Langmuir			Freundlich		
	Q (mg/g)	b (l/mg)	Correlation Coefficient (R^2)	K_F	n	Correlation Coefficient (R^2)
Phenol	11.765	0.006	0.944	0.1513	1.346	0.996
2-Chlorophenol	16.129	0.012	0.834	0.4446	1.517	0.981

Table 2 shows the Langmuir and Freundlich isotherm model for the adoption of phenol and 2-cholorophenol using activated carbon. Both models were used to explain the relationship between the amount of phenol and 2-clholorophenolradsorbed and corresponding to the equilibrium concentration. A failure of the Langmuir isotherm model has been describe for the separation factor R_L. The Langmuir model can be expressed as following equation.

$$R_L = \frac{1}{(1 + KC_0)}$$

Where Co is the highest initial concentration, K is Langmuir's adsorption constant. This parameter indicates as the following ways: unfavorable if RL > 1, linier if RL = 1, favorable if 0<RL<1, or irreversible if RL = 0. In this investigation, adsorption phenol using activated carbon was favorable and R2 value is 0.944 proving the sorption data well fitted to follow Langmuir model. However, adsorption 2-chlorophenol was 0.834. The linier form of the Freundlich isotherm model show that R^2 values of phenol and 2-chlorophenol are 0.996 and 0.981, respectively. The R^2 values show that both Langmuir and Freundlich isotherm model exhibited well adsorption model behavior of phenol and 2-chlorophenol[18].

4. Conclusion

Activated carbon prepared from oil palm shell was successfully obtained by physical activation and nitric acid. Textural properties of activated carbon involves surface area, predominantly microporous structure and pore diameter < 0.2nm. Phenol and 2-chlorophenol were successfully removed by the activated carbon. The adsorption capacity was considerably affected by pH, mass of activated carbon and contact time. Equilibrium study indicated that the Langmuir and Freundlich isotherm model favorably describe for the adsorption phenol, while the Freundlich isotherm model favorably describes for the 2-chlorophenol.

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