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Equilibrium, Kinetic and Thermodynamic Studies of Analgesic Removal by Thin Coated Activated Carbon

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Abstract: *Acetaminophen (analgesic) also known as paracetamol, usually used to reduce moderate pain such as headaches, menstrual periods, cold/flu aches and fever. This is one of the pharmaceutical products generally consume and dispose to the environment and become pharmaceutical pollution. This research, study a new approach applying adsorption concept. Thin coated activated carbon (TCAC) for adsorption of acetaminophen was investigated. The TCAC is formulated using Epoxidised Neutral Rubber (ENR-50) and poly(vinyl) chloride (PVC) as binders with activated carbon as an adsorbent, then was coated on white cotton fabric via brushing technique. Characterisation analysis using Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) and Brunauer–Emmett–Teller (BET) analysis were performed. The pore volume and surface area of the TCAC are 0.07 $cm^3\ g^{-1}$ and 64.3 $m^2\ g^{-1}$, respectively. The TCAC was evaluated through varies parameters including different initial concentrations and temperatures. The amount of acetaminophen as adsorbate, 50 mg L^{-1}, able to be adsorbed up to 32.43 mg g^{-1} into TCAC within 5 h. The result of equilibrium and kinetic studies indicated that Langmuir isotherm model and pseudo-second-order, respectively, are best fitted the adsorption of acetaminophen onto TCAC. It was decisive that the adsorption process of acetaminophen on TCAC is spontenoous ($\Delta G° < 0$) and exothermic ($\Delta H° < 0$) through thermodynamic studies.*

Keywords: analgesic, acetaminophen, TCAC, thin coated activated carbon, activated carbon, adsorption

1. INTRODUCTION

Pharmaceutical emerging pollutant considered as rare pollutants has been detected nowadays. This kind of pollutant has attracted much attention among researchers because of growing pharmaceutical manufacturing industries and human behaviour. There are few categories listed under pharmaceutical emerging pollutants have been detected which are antibiotic, analgesic, antiepileptic, dopamine, opioids, antiseptics, steroid hormones and stimulant.[1] However, the most common categories has been found in water stream is analgesic. Under analgesic categories there are several compound been highlighted which are acetaminophen, codeine, ibuprofen and naproxen.[2] In the United States, it was reported detection frequency exceeding 30% of the water stream from 47 groundwater sites selected.[3] Then, wastewater sample has been collected from five different types of sewage treatment plants in Johor, Malaysia.[1] There are nine pharmaceutical compounds (acetaminophen, lincomycin, trimethoprim, sulfamethazine, sulfamethoxazole, clarithromycin, carbamazepine, ibuprofen, and naproxen) that are the most frequently consumed by resident living nearby of these sewage treatment plant. Acetaminophen was recorded the highest concentration has been detected able to reach 40.17 mg L^{-1}. Consequent of that all of the pharmaceutical compounds are potentially harmful to the aquatic organisms and human life in the future. These substances enter the environment largely from wastewater treatment, aquaculture treatment and leaking landfills.[4,5] Other exposure pathways exist, including emission from manufacturing industries, disposal of unused medicine to landfill and flushed down the toilet, irrigation with wastewater from hospitals, veterinary medicine from the hard surface in farmyards and disposal of carcasses of treated animals.[6–8] Other than that, this pollutant is able to enter the environment when a person who takes medicine, up to 9% of medicine excreted out of the body through urination, then it flushed down the toilet and mixed with wastewater.[9]

In Malaysia, pharmaceutical waste from hospital, clinic and any medical store has been regulated under government on disposal of expired, unused and defected medicine through Environmental Quality (Scheduled Waste) Regulation 2005. However, this regulation does not apply to residencies, aquaculture activities and others, where there has an irresponsible citizen that disposed the medicine improper ways to landfills and also mixed together with their daily food waste, then disposed in flushing bowls. Through that pathway, it showed how easy this pollutant may enter the environment. The pollutant concentration stated by a group of researchers in Johor, Malaysia, frequently detected.[2] Moreover, these compounds with long-term exposure may lead to mutagenic and genotoxic effects on aquatic

life. As a consequence, the compounds drastically decrease the reproductive success in aquatic life. The most critical effect arises from the exposure to these compounds is their ability to cause the liver and reproductive damage in human health, accumulation tissues and inhibition of cell proliferation.[10]

By disposing the medicine in toilet bowls, it will eventually ended up in sewage treatment plant. Unfortunately, the treatment plant did not have any specific treatment for pharmaceutical waste. So, the water will not be treated accordingly before discharged and distributed back to the residents. According to previous research, there are several conventional sewage treatment processes to facilitate in removal of these compounds, such as coagulation, sedimentation, filtration but it inefficient because only able to remove about 10% to 20% of these compounds.[11] Nowadays, domestic sewage treatment is using biological treatment systems. In Malaysia, commonly included extended aeration, oxidation ditch, oxidation pond, sequencing batch bioreactor. The biological treatment system is a reliable treatment system especially in removing high organic and nutrient content from sewage.[12] However, it is still not completely eliminate the pollutants before distributed to residents.[2]

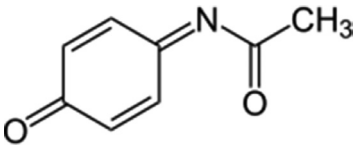
Presently, this research is aimed to develop a novel adsorption technology that will reduce the amount of pharmaceutical pollutant exist in the environment. The existing adsorption process requires several types of equipment to operate such column, pump, valve and need energy consumption to run the system. In this research study, the technology is relatively simple to be applied in the wastewater treatment system. It can be added onto the existing process without affecting their current operation. Therefore, the performance of TCAC being investigated in the application of acetaminophen removal from the aqueous solution.

2. MATERIALS AND METHODS

2.1 Chemicals

Acetaminophen was purchased from BT Science Sdn. Bhd. The chemical structure and physical properties of acetaminophen are shown in Table 1.[13] Epoxidised Neutral Rubber with 50% mol of epoxidation (ENR-50) was provided by School of Chemistry, Universiti Sains Malaysia. Toluene and dichloromethane were supplied by BT Science Sdn. Bhd. PVC, commercial untreated activated carbon and kaolinite were obtained from Sigma-Aldrich Sdn. Bhd.

Table 1: Properties and chemical structure of acetaminophen.

Chemical structure	
Category	Analgesics
IUPAC name	N – (4-hydroxyphenyl) acetamide
Molecular weight	151.165 g mol^{-1}
Odour	Odourless
Colour	White powder
Taste	Slightly bitter
Melting point	168°C
Solubility	> 22.7 µg mL^{-1}

2.2 Preparation of Adsorbate

The stock solution of adsorbate (Acetaminophen) was prepared before the experiment started by weighing 0.4 g of acetaminophen using analytical balance (A&D Company, Limited, model HR-250A) and completely dissolved into 2 L of distilled water. The stock solution was then diluted to several studied concentrations. The dilution is calculated using Equation 1. The detection of adsorbate via UV-vis spectroscopy, the calibration curve of acetaminophen have been created with wavelength 287 nm respectively through various concentration (1, 10, 20, 30, 40, 50 and 100 mg L^{-1}).

$$M_1V_1 = M_2V_2 \quad (1)$$

Where:

M_1 = Concentration of stock solution (200 mg L^{-1})
V_1 = Volume of stock solution need to be diluted (L)
M_2 = Concentration required (mg L^{-1})
V_2 = Volume need to be tested (L)

2.3 Preparation of Thin Coated Activate Carbon (TCAC)

ENR-50 solid was dissolved using the reflux process, where 24.80 g of solid ENR-50 was mixed with 250 mL of toluene. Then, the mixture was left for reflux under the temperature of 85°C to 90°C for 80 h.[14] After that, 0.80 g of PVC

in 35 mL of dichloromethane was dissolved via sonication for 30 min. Then, 4 g of ENR-50 solution was mixed with 65 mL toluene and the mixture was shaken for 1 min. Next, 4 g of activated carbon was added and the mixture was sonicated for 6 h.[15] After being sonicated, the mixture was divided into 6 mL for each coating. The solution was applied onto a cotton fabric (dimension 210 mm × 50 mm) via brushing technique, and dried in the oven at 100°C for 5 min.

2.4 Batch Adsorption Studies

The acetaminophen solution was prepared from a stock solution (200 mg L^{-1}). The adsorption performance was evaluated through various initial concentrations (5 to 100 mg L^{-1}) and temperature (30°C, 40°C and 50°C). The TCAC strip was weighed prior to the testing. Then, the strip was placed to the interior wall of 250 mL beaker and adsorption process start. The sample solution was collected for every 30 min interval and analysed it. The experiment was continued for 5h. The adsorption isotherm study was performed applying the recorded experimental results.

The equilibrium adsorption values were calculated using the equations below. The amount of acetaminophen adsorbed, q_t (mg g^{-1}) on the coated strip at a particular temperature was determined using Equation 2:

$$q_t = \frac{(C_0 - C_t)}{W} \tag{2}$$

where C_0 and C_t (mg L^{-1}) are initial concentration of acetaminophen and concentration at the time t, respectively. V is the volume (in L) is the volume of acetaminophen solution that has been tested and W is the mass (in gram) of adsorbent used for each coating.

The equilibrium adsorption capacity (q_e) was determined according to the following equation, Equation 3:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{3}$$

2.5 Adsorption Isotherm Studies

The nature of adsorbent coating toward the adsorption of acetaminophen was examined through Langmuir, Freundlich and Temkin isotherm models.

2.5.1 Langmuir adsorption isotherm

The Langmuir isotherm is the most common and very popular model used by researchers in order to quantify the amount of adsorbate on an adsorbent as a function of particular concentration at a given temperature. Basic theoretical assumes monolayer coverage of adsorbate and takes place homogenous site of adsorbent surface. Therefore, at equilibrium, a saturation point is reached where no further interaction can occur, once the adsorbate molecule occupied a site.[16] The equation as calculated using Equation 4:[17]

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4}$$

The separation factor (R_L) is used to evaluate if the adsorption if unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$), R_L can be calculated as:[18]

$$R_L = \frac{1}{1 + K_L C_O} \tag{5}$$

2.5.2 Freundlich adsorption isotherm

The Freundlich isotherm was practised for adsorption on heterogenous surface energy system where the binding site is not equivalent. This model is describing the adsorption is multilayer adsorption of adsorbate and heterogeneous of adsorbent surface.[19] Adsorption intensity or surface heterogeneity becoming more heterogeneous as its value gets closer to zero. The equation of Freundlich isotherm as calculated using equation below:[20]

$$q_e = k_F (C_e)^{1/n} \tag{6}$$

2.5.3 Temkin adsorption isotherm

Temkin isotherm model studied the heat of adsorption and the adsorbate-adsorbent interaction on adsorption. By ignoring the extremely low and large value of concentration, the model assumes that heat od adsorption of all molecules in the layer would decrease linearly that logarithmic with coverage.[21] The equation Temkin is calculated using Equation 7[22] where related parameters are defined in Table 2. R represents the universal gas constant (8.314 J mol.K^{-1}) and T is absolute temperature in Kelvin.

$$q_e = \left(\frac{RT}{b}\right) \ln(k_T C_e) \tag{7}$$

Table 2: Parameters and definition of isotherm models.

Parameter	Definition
C_O	Initial concentration (mg L^{-1})
C_e	Concentration at equilibrium state (mg L^{-1})
	Langmuir Model
q_m	Maximum adsorption capacity (mg g^{-1})
k_L	Langmuir isotherm constant (L mg^{-1})
	Freundlich Model
k_F	Freundlich isotherm constant (mg g^{-1}. (L $mg^{-1})^{1/n}$)
n	Adsorption intensity
	Temkin Model
k_T	Temkin isotherm equilibrium binding constant (L mg^{-1})
b	Constant related to the heat of adsorption (J mol^{-1})

2.6 Error Analysis

The optimisation procedure requires an error function to be defined in order to evaluate the best fit of the isotherm to experimental equilibrium data. The correlation coefficient for non-linear, r^2 (close to 1) was solved using Solver Microsoft Excel, as calculated using Equation 8. Error function was calculated for all isotherm models and those with the lowest value of error analysis was selected as the best model to describe the experimental data. In this study, Average Relative Error (ARE) was used as Equation 9.

$$r^2 = \frac{\sum (q_{e,cal} - q_{e,ave})^2}{\sum (q_{e,cal} - q_{e,ave})^2 + \sum (q_{e,cal} - q_{e,exp})^2} \tag{8}$$

$$ARE = \sum \left| \frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right| \tag{9}$$

where $q_{e,exp}$ (mg g^{-1}) and $q_{e,\ cal}$ (mg g^{-1}) are the adsorption capacity from experimental data and calculated from the model, respectively. While $q_{e,ave}$ (mg g^{-1}) is represent as average adsorption capacity.

2.7 Kinetic Studies

In 1898, Lagergren's kinetics equation was the first one in describing the adsorption of a liquid-solid system based on solid capacity. The first order rate equation is also known as pseudo-first-order.[23] The equation is presented as Equation 10:

$$\log (q_e - q_t) = \log q_e - \frac{k}{2.303} t \tag{10}$$

where q_e, equilibrium adsorption capacity (mg g^{-1}), q_t is the adsorption capacity (mg g^{-1}) at time t (min) and K is the constant of pseudo-first-order rate (1 min^{-1}). The constants of pseudo-first-order can be defined by plotting log ($q_e - q_t$) against t.

In 1999, Ho and McKay proposed a pseudo-second-order equation that explained the amount of adsorbate captured on the adsorbent.[24] The pseudo-second-order is a chemisorption equation and the non-linear equation was expressed by Equation 11:

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

where q_t and q_e is the amount of adsorption capacity (mg g^{-1}) at time t (min) and at equilibrium, respectively. Then, K_2 is the rate constant of the pseudo-second-order equation (g mg.min^{-1}). The constant of pseudo-second-order kinetic can be defined by plotting t q_t^{-1} against t.

2.8 Thermodynamic Studies

Thermodynamic parameter such as standard enthalpy ΔH°, entropy change ΔS° and Gibbs free energy change ΔG° are studied to evaluate the feasibility of the adsorption process. The experiments are evaluated based on different temperature (303, 313 and 323 K). The thermodynamic value was calculated with the following equations:[25]

$$\Delta G° = - RT \ln k_L \tag{12}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{13}$$

$$\ln k_L = - \frac{-\Delta H°}{R} \frac{1}{T} + \frac{\Delta S°}{R} \tag{14}$$

$$k_L = \frac{q_e}{C_e} \tag{15}$$

where, R is the universal gas constant (8.314 J mol. K^{-1}), T is the absolute temperature in Kelvin (K) and k_L is equilibrium constant. The linear graph is plotted ln k_L against 1/T. ΔH° and ΔS° are determined from the slope and intercept of the graph respectively. Then, ΔG° is calculated using Equation 13 with varies temperatures (303, 313 and 323 K).

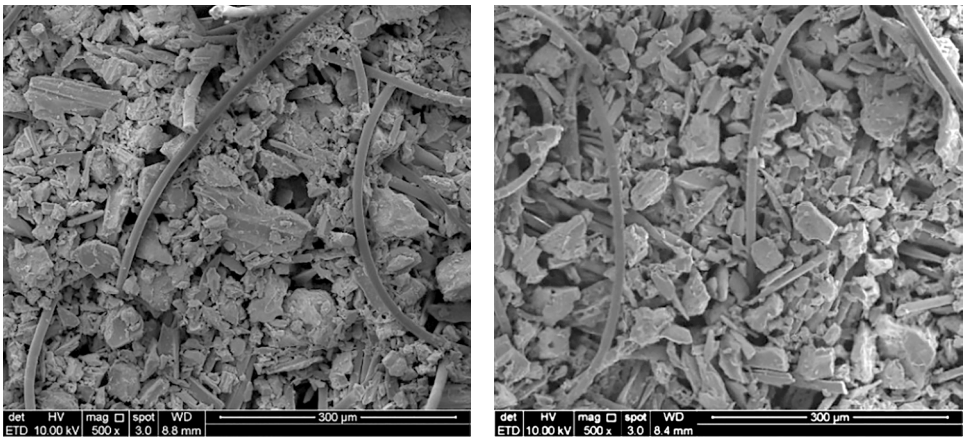
2.9 Apparatus and Instrumentation

The apparatus used were 250 mL beaker, magnetic stirrer and cuvette (Quartz material). A magnetic stirrer (Multi Hotplate Stirrer WISD Laboratory Instrument SMHS-6) was used for mixing the slurry and adsorbate homogeneously. The UV-vis, spectrophotometer (Shimadzu UV-1800) was employed to measure the concentration of acetaminophen. The coating solution was dissolved by sonication process (model Elmasonic S80H). Drying oven (Constance Germany) was used to dry the TCAC. The surface morphology and content of the elements in TCAC was evaluated by using Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) spectroscopy (model Crest System (M) Sdn. Bhd. Quanta Feg 450). For BET analysis, a piece of TCAC (dimension 10 mm × 30 mm) was tested. The surface area, total pore volume and pore size of the TCAC and commercial AC were determined in nitrogen adsorption isotherm at 77 K using a BET surface analyser (Micromeritics model ASAP 2000, Nocross, GA).

3. RESULTS AND DISCUSSION

3.1 Characterisation

The scanning electron microscopy analysis captured the images of surface morphology of TCAC for before and after adsorption as illustrated in Figure 1. The activated carbon fully coated on white cotton fabric. The adsorbent with varies size was strongly attached through binder (ENR-50 and PVC). There is a huge amount of small particle of activated carbon, therefore, the surface area for adsorption can be increased. No obvious sign of acetaminophen attached to the TCAC, but it has been proven through EDX analysis. The main elements representing the compound of ENR-50, PVC and activated carbon which is carbon, oxygen, and chloride detected in high amounts as illustrated in Figure 2(a) and 2(b). Table 3 was summarised as the weight percentage of the elements. The nitrogen (2.14%) has been detected which indicated the element of acetaminophen compound as shown in Figure 2(b). Therefore, it is proven there is an interaction between the acetaminophen and the surface of TCAC. The result of BET analysis demonstrated that the surface area of commercial AC decreased drastically when it introduced in TCAC (948.1 $m^2\ g^{-1}$ to 64.3 $m^2\ g^{-1}$). A similar pattern also observed in pore volume analysis, where the decreasing values from 0.94 $cm^3\ g^{-1}$ to 0.07 $cm^3\ g^{-1}$. However, there is some increment in pore size diameter from 39.6 Å to 45.1 Å. According to the research by Bahrudin and Nawi (2017), similar trends of decreasing surface area and pore volume whilst the pore size diameter is increasing when ENR-50 and PVC were introduced as a coating.[15]

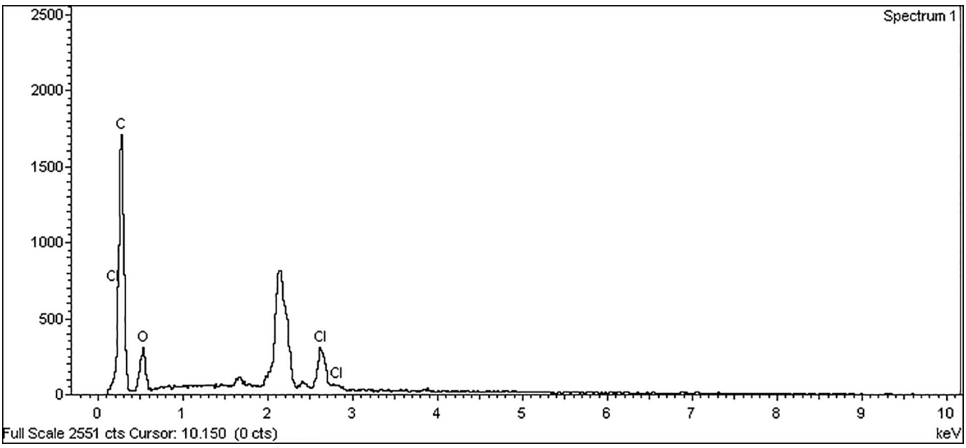


(a) (b)

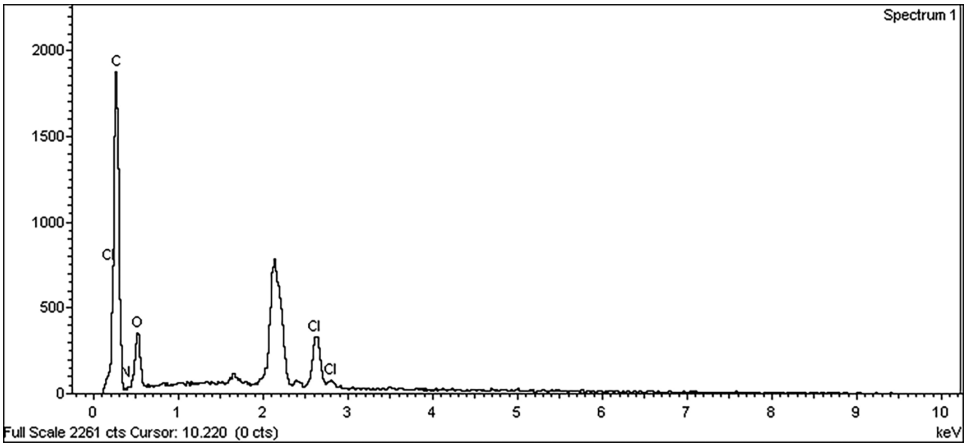
Figure 1: SEM images of TCAC (a) before (Mag. ×500) and (b) after adsorption process (Mag. ×500).

3.2 Adsorption Isotherm Studies

Table 4 summarised the adsorption isotherm models for Langmuir, Freundlich and Temkin for the TCAC at 30°C and Figure 3 showed the plotted graph of comparison non-linear isotherm models. The data show obvious distinction among all the three models. The data were obtained from the experiments, it showed that Langmuir model was the best fitted which determined through correlation coefficient (r^2), where the values for Langmuir model (0.999) were higher than Freundlich and Temkin models, 0.0.764 and 0.796 respectively. However, this result was supported by error analysis which are Langmuir (0.05), Freundlich (0.97) and Temkin (1.72). Therefore, the result proved Langmuir isotherm models is the best fitted isotherm or adsorption process of TCAC onto acetaminophen. Langmuir model indicates the adsorption is monolayer coverage of these adsorbates on the surface of TCAC and take place at specific homogenous site on the adsorbent, where no further adsorption can occur when a site is occupied with adsorbate.[26] The other main characteristic of Langmuir isotherm can be expressed by dimensionless constant called equilibrium parameter, R_L which indicates the type of isotherm. The R_L value between 0 and 1 indicates favourable adsorption, ($R_L > 1$) is unfavourable, ($R_L = 1$) is linear and ($R_L = 0$) is irreversible.[27] According to the results, the adsorption of acetaminophen onto TCAC has shown a favourable process by having RL value was 0.87.



(a)



(b)

Figure 2: EDX analysis (a) before and (b) after adsorption.

Table 3: The weight percentage of elements detected from EDX analysis.

Items	Elements weight percentage (wt. %)			
	Carbon, C	Oxygen, O	Chloride, Cl	Nitrogen, N
Before	76.01	11.88	12.12	–
After	72.13	15.46	10.27	2.14

Table 4: Summary of adsorption isotherms.

Models		Langmuir			Freundlich			Temkin		
C_e (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	ARE	r^2	$q_{e,cal}$ (mg g^{-1})	ARE	r^2	$q_{e,cal}$ (mg g^{-1})	ARE	r^2
4.63	1.35	1.38			1.35			1.35		
19.63	8.76	8.92			8.76			20.61		
29.35	32.43	34.43	0.05	0.999	14.75	0.97	0.796	25.97	1.72	0.796
50.16	37.87	37.71			29.55			33.12		
73.38	40.13	39.89			48.38			38.19		

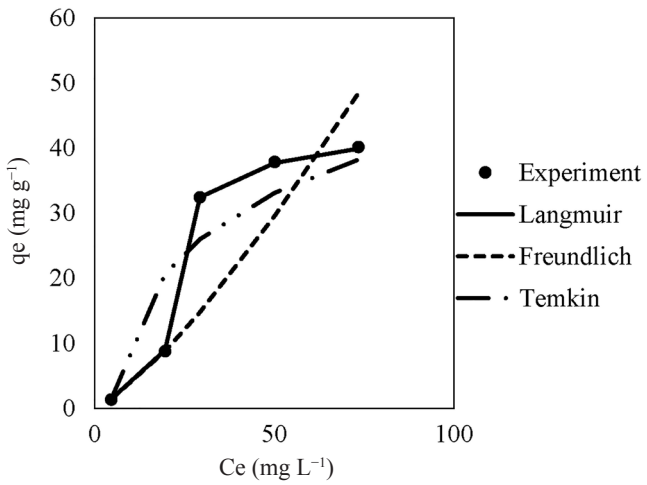


Figure 3: Comparison non-linear for Langmuir, Freundlich and Temkin isotherm models at 30°C.

3.3 Adsorption Kinetic Studies

The adsorption kinetics of acetaminophen onto TCAC were evaluated through pseudo-first-order and pseudo-second-order models on the data that was obtained from the experimental studies. The results were tabulated in Table 5. From the data, it shows that pseudo-second-order has higher correlation coefficient, (R^2 = 0.935 to 0.998) compared to pseudo-first-order (R^2 = 0.468 to 0.947). Moreover, the adsorption capacity calculated ($q_{e,\,cal}$) value agree with the experimental data ($q_{e,\,exp}$). The data also supported by ARE, the result obtained were 2.45 and 3.13 for pseudo-second-order and pseudo-first-order, respectively. Therefore, the result approved that adsorption is well described by the pseudo-second-order kinetic model. It means the chemisorption mechanism and

having strong interaction between the adsorbate and adsorbent. The adsorption mechanism may involve force through electron sharing or exchanged between TCAC and the adsorbate.[28]

Table 5: Pseudo-first-order, pseudo-second-order constants and R^2 values for adsorption of acetaminophen on TCAC at 30°C.

Initial dye concentration (mg L^{-1})	$q_{e\ exp}$ (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
		$q_{e\ cal}$ (mg g^{-1})	K (1 min^{-1})	R^2	$q_{e\ cal}$ (mg g^{-1})	K_2 (1 min^{-1})	R^2
5	1.35	1.81	0.0180	0.468	3.12	0.0079	0.961
25	8.76	1.70	0.0196	0.947	16.31	0.0007	0.935
50	32.43	13.30	0.0246	0.821	27.78	0.0018	0.995
75	37.87	14.22	0.0244	0.830	33.89	0.0023	0.998
100	40.13	9.26	0.0290	0.671	41.15	0.0036	0.991

3.4 Thermodynamic Studies

Through the effect of temperature adsorption thermodynamic can be determined by varies temperature (303, 313 and 323 K). The Gibb's energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were the parameters for thermodynamic studies and were determined through Equations 12 to 15. The results were shown as $\Delta S° = -0.95$ kJ $mol.K^{-1}$ and $\Delta H° = -324.16$ J mol^{-1}, the negative values obtained implies the adsorption process was exothermic process. This was the process where the energy was released into its surrounding.[29] The values of ΔG° (−34.96, −25.41 and −15.87 kJ mol^{-1}) were more towards negativity as temperature rises which were 303, 313 and 323 K respectively. According to the negative values of ΔG°, ΔS° and ΔH°, it is proven that the process is spontaneous and exothermic. The results are comparable with other researcher.[30]

4. CONCLUSION

As a conclusion, it was proven that TCAC is adsorbing acetaminophen with 32.43 mg g^{-1} of adsorption capacity. The equilibrium studies, adsorption kinetic and thermodynamic studies were examined using various initial concentrations and temperatures. As a result, it showed that the Langmuir model is best fitted for this adsorption of acetaminophen onto TCAC through correlation coefficient with supported by smallest error analysis. The Langmuir model indicated monolayer coverage and homogenous site on the adsorbent. Moreover, kinetic studies showed pseudo-second-order is well presented by the adsorption process. Thermodynamic

studies found that Gibbs energy, ΔG° is more negativity as all temperature rises from 303 to 323 K, while both ΔH° and ΔS° were also negative value. This reflects that the process is spontaneous and exothermic. The innovative approach in this research, by introducing the TCAC as a medium for the adsorption process is relevant for research nowadays.[31]

5. ACKNOWLEDGEMENTS

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