Pharmaceutical Emerging Pollutant Removal by Thin Activated Carbon Coating: Equilibrium, Kinetic, and Thermodynamic Studies

Muhamad Sharafee Shamsudin¹, Suzylawati Ismail¹*
¹School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300, Nibong Tebal, Pulau Pinang, Malaysia.

E-mail: chsuzy@usm.my

Abstract. In Malaysia, issues of pharmaceutical pollutant have been highlighted recently. Acetaminophen (analgesic) also known as paracetamol that usually used to reduce moderate pain such as headaches, menstrual periods, cold/flu aches and fever. There are a large amount of acetaminophen has been detected in sewage treatment plants in Malaysia. Unfortunately, sewage treatment plants are not effective enough to overcome this kind of pollutant. Therefore, in this research study, a new approach applying adsorption concept is introduced. Thin activated carbon coating (TACC) for adsorption of acetaminophen (ACT) was investigated. The TACC is formulated using Epoxidized 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. Characterization analysis using SEM-EDX and BET analysis were performed. The pore volume and surface area of the TACC are 0.07 cm³/g and 64.3 m²/g, respectively. The TACC was evaluated through varies parameters including different initial concentrations and temperatures. The amount of ACT as adsorbate, 50 mg/L, able to be adsorbed up to 33.3 mg/g into TACC within 5 h. The result of equilibrium and kinetic studies indicated that Freundlich isotherm model and pseudo-second-order, respectively, are best fitted the adsorption of ACT onto TACC. It was decisive that the adsorption process of ACT on TACC is spontaneous (∆G⁰ <0) and exothermic (∆H⁰ <0) through thermodynamic studies.

1. Introduction
Pharmaceutical emerging pollutant considered as rare pollutants has been detected nowadays. This kind of pollutant has attracted much attention among the researchers because of growing

* To whom any correspondence should be addressed
pharmaceutical manufacturing industries and human behavior. In the United States, it was reported detection frequency exceeding 30% of the water stream from 47 groundwater sites selected [1]. Then, wastewater sample has been collected from five different types of sewage treatment plants in Johor, Malaysia [2]. There are six pharmaceutical compounds (Acetaminophen, Lincomycin, Trimethoprim, Sulfamethazine, Sulfamethoxazole, Clarithromycin, Carbamazepine, Ibufrofen, and Naproxen) 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. 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 [3][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 animal [6][7][8]. Other than that, this pollutant able to enter the environment is when a person who takes medicine, up to 9 percent 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].

The disposal of medicine through flushing in toilet bowls, therefore it directly been through sewage wastewater 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 – 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 TACC being investigated in the application of acetaminophen removal from the aqueous solution.

2. Experimental

2.1 Materials

Acetaminophen (ACT) was purchased from BT Science Sdn. Bhd. The chemical structure and physical properties of ACT are shown in Table 1. Epoxidized 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. Poly(vinyl) chloride, commercial untreated activated carbon and kaolinite were obtained from Sigma-Aldrich Sdn. Bhd.

| Table 1. Properties and chemical structure of acetaminophen [13] [14]. |
|-------------------------------------------------------------|
| Chemical structure |
| Category         | Analgesics           |
| IUPAC name       | N – (4-hydroxyphenyl) acetamide |
| Molecular weight | 151.165 g/mol         |
| Odor             | Odorless             |
| Color            | Large monoclinic prisms from water |
| Taste            | Slightly bitter      |
| Melting point    | 168 ℃               |
| Solubility       | > 22.7 µg/mL         |

2.2 Preparation of adsorbate
The stock solution of adsorbate (ACT) was prepared before the experiment started by weighing 0.4 g of ACT 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 ACT have been created with wavelength 287 nm respectively through varies concentration (1, 10, 20, 30, 40, 50 and 100 mg/L).

\[ M_1V_1 = M_2V_2 \]  

(1)

Where:
- \( M_1 \) = Concentration of stock solution (200 mg/L)
- \( V_1 \) = Volume of stock solution need to be diluted (L)
- \( M_2 \) = Concentration required (mg/L)
- \( V_2 \) = Volume need to be tested (L)

2.3 Preparation of Thin Activate Carbon Coating (TACC)
Epoxidized Neutral Rubber (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 – 90 ℃ for 80 hours [15]. 0.80 g of poly(vinyl) chloride (PVC) in 35 ml of dichloromethane was dissolved via sonication for 30 minutes. Then, 4 g of ENR-50 solution was mixed with 65 mL toluene and the mixture was shaken for 1 minute. Next, 4 g of activated carbon was added and the mixture was sonicated for 6 hours [16]. After being sonicated, the mixture was divided into 6 mL for each coating. The solution was applied onto a cotton fabric (dimension 210 mm x 50 mm) via brushing technique, and dried in the oven at 100 ℃ for 5 minutes.

2.4 Batch adsorption studies
The acetaminophen solution was prepared from a stock solution (200 mg/L). The adsorption performance was evaluated through various initial concentrations (5 to 100 mg/L) and temperature (30, 40, 50, 60 and 70℃). The TACC 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 analyzed 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 ACT adsorbed, $q_t$ (mg/g) on the coated strip at a particular temperature was determined using Eq. (2):

$$q_t = \frac{(C_0 - C_t)V}{W}$$  \hspace{1cm} (2)

where $C_0$ and $C_t$ (mg/L) are initial concentration of ACT and concentration at the time $t$, respectively. $V$ is the volume (in L) is the volume of ACT 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, Eq. (3):

$$q_e = \frac{(C_0 - C_e)V}{W}$$  \hspace{1cm} (3)

### 2.5 Adsorption isotherm studies

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

#### 2.5.1. Langmuir adsorption isotherm

The nature of ACT adsorption (homogeneous monolayer) on the surface of the adsorbent coating was examined using the Langmuir isotherm [17]. The Langmuir adsorption isotherm is shown as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_L q_mC_0}$$  \hspace{1cm} (4)

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

$$R_L = \frac{1}{1 + k_L C_0}$$  \hspace{1cm} (5)

#### 2.5.2 Freundlich adsorption isotherm

Heterogeneous and multilayer surface adsorption can be described using the Freundlich model [19]. The equations of Freundlich isotherm are:

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

$$\ln q_e = \ln k_F + \left(\frac{1}{n}\right) \ln C_e$$  \hspace{1cm} (7)

Where:

| Table 2. Parameters and definition of isotherm models. |
|-------------------------------------------------------|
| **Parameter** | **Definition**                                      |
|---------------|-----------------------------------------------------|
| $C_0$         | Initial concentration (mg/L)                        |
| $C_e$         | Concentration at equilibrium state (mg/L)           |
| $q_m$         | Maximum adsorption capacity (mg/g)                  |
| $k_L$         | Langmuir isotherm constant (L/mg)                   |
| $k_F$         | Freundlich isotherm constant (mg/g. (L/mg)$^{1/n}$) |
| $n$           | Adsorption intensity                                 |
2.6 Error analysis
The optimization procedure requires an error function to be defined in order to evaluate the best fit of the isotherm to experimental equilibrium data. 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, linear coefficient of determination and non-linear the Chi-square test ($\chi^2$), root mean square error (RMSE) and sum of error squares (SSE) were used.

Chi-square test ($\chi^2$) [20] value was evaluated using the Eq. (8):

$$\chi^2 = \sum_{i=1}^{n} \frac{(q_{e,cal} - q_{e,exp})^2}{q_{e,exp}}$$  \hspace{1cm} (8)

Residual root mean square error (RMSE) [21] was determined using the Eq. (9):

$$RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^{n} (q_{e,exp} - q_{e,cal})^2}$$  \hspace{1cm} (9)

Sum of error squares (SSE) [22] analysis was examined using the Eq. (10):

$$SSE = \sqrt{\frac{\sum_{i=1}^{n} (q_{e,exp} - q_{e,cal})^2}{n}}$$  \hspace{1cm} (10)

Where $q_{e,exp}$ (mg/g) and $q_{e,cal}$ (mg/g) are the adsorption capacity from experimental data and calculated from the model, respectively. Then, $n$ is the number of data used.

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 (Ho, 2004). The equation is presented as Eq. (11):

$$\log(q_e - q_t) = \log q_e - \frac{K}{2.303} t$$  \hspace{1cm} (11)

Where $q_e$, equilibrium adsorption capacity (mg/g), $q_t$ is the adsorption capacity (mg/g) at time $t$ (min) and $K$ is the constant of pseudo-first-order (1/min). 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 nonlinear equation was expressed by Eq. (12):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (12)

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

2.8 Thermodynamic studies
Thermodynamic parameter such as standard enthalpy $\Delta H^o$, entropy change $\Delta S^o$ and Gibbs free energy change $\Delta G^o$ are studied to evaluate the feasibility of the adsorption process. The experiments are evaluated based on different temperature (303, 313, 323, 333 and 343 K). The thermodynamic value was calculated with the following equations [25]:

$$\Delta H^o = \frac{n C_p \Delta T}{n C_p \Delta T}$$

$$\Delta G^o = \Delta H^o - T \Delta S^o$$
\[ \Delta G^\circ = -RT \ln K_d \]  \\
[13] \\
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]  \\
[14] \\
\[ \ln K_d = \frac{-\Delta H^\circ}{R} + \frac{\Delta S^\circ}{R} \]  \\
[15] \\
\[ K_d = \frac{q_d}{C_d} \]  \\
[16] 

Where, R is the universal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin (K) and \( K_d \) is equilibrium constant. The linear graph is plotted \( \ln K_d \) against 1/T. \( \Delta H^\circ \) and \( \Delta S^\circ \) are determined from the slope and intercept of the graph respectively. Then, \( \Delta G^\circ \) is calculated using Eq. 14 with varies temperatures (303, 313, 323, 333 and 343 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 ACT. The coating solution was dissolved by sonication process (model Elmasonic S80H). Drying Oven (Constance Germany) was used to dry the TACC. The surface morphology and content of the elements in TACC was evaluated by using Scanning Electron Microscope – Energy Dispersive X-ray spectroscopy (SEM-EDX) spectroscopy (model Crest System (M) Sdn. Bhd. Quanta Feg 450). For BET analysis, a piece of TACC (dimension 10 mm x 30 mm) was tested. The surface area, total pore volume and pore size of the TACC and commercial AC were determined in nitrogen adsorption isotherm at 77 K using a BET surface analyzer (Micromeritics model ASAP 2000, Nocross, GA).

3. Results and Discussion
3.1. Characterization
The Scanning Electron Microscopy analysis captured the images of surface morphology of TACC 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 ACT attached to the TACC, but it has been proven through energy dispersive x-ray analysis. The main elements representing the compound of ENR-50, PVC and activated carbon which is carbon, oxygen, and chloride detected in high amounts which weigh percentage 72.13%, 15.46% and 10.27%, respectively, as illustrated in Figure 2(a) and 2(b). The nitrogen (2.14%) has been detected which indicated the element of ACT compound [13] as shown in Figure 2(b). Therefore, it is proven there is an interaction between the ACT and the surface of TACC. The result of BET analysis demonstrated that the surface area of commercial AC decreased drastically when it introduced in TACC (948.1 m²/g to 64.3 m²/g). A similar pattern also observed in pore volume analysis, where the decreasing values from 0.94 cm³/g to 0.07 cm³/g. However, there is some increment in pore size diameter from 39.6 Å to 45.1 Å. According to the research by Bahrudin & 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 [16].
Figure 1. SEM images of TACC (a) before (Mag. x500) and (b) after adsorption process (Mag. x500).

Figure 2. Energy Dispersive X-ray (EDX) analysis (a) before and (b) after adsorption.

3.2. Adsorption isotherm studies
Table 3 summarising the adsorption isotherm models for Langmuir and Freundlich for the TACC at 30°C. The data were obtained from the experiments, it showed that Freundlich model was the best fitted which determined through correlation coefficient ($R^2$), where the values for Freundlich model were higher than Langmuir model, 0.9183 and 0.9073 respectively. However, this result was
supported by error analysis as showed in Table 4. There was a comparison of $R^2$ value on non-linear regression with other error function. As the evaluation for Freundlich isotherm is showing the coefficient of determination, $R^2$ was slightly higher as compared to Langmuir isotherm, then error function obviously the smallest value. The Freundlich model is associated with a heterogeneous and multilayer surface adsorption, which would relate to more selective adsorption [26]. Therefore, for the adsorption process of ACT onto TACC, Freundlich isotherm is the best-fitted model.

Table 3. Summary of parameters from linear adsorption isotherms

|             | Langmuir Isotherm | Freundlich Isotherm |
|-------------|-------------------|---------------------|
| $R^2$       | 0.9073            | 0.9183              |
| $q_m$ (mg/g)| 103.092           | 1/n                 |
| $k_L$ (L/mg)| 0.01102           | n                   |
| $R_L$       | 0.6447            | $k_F$ (mg/g. (L/mg)${}^{1/n}$) | 3.8126 |

Table 4. Comparison of the non-linear regression

|             | Langmuir Isotherm | Freundlich Isotherm |
|-------------|-------------------|---------------------|
| SSE         | 4.6673            | 3.4266              |
| $\chi^2$   | 3.0808            | 1.9390              |
| RMSE        | 6.0254            | 4.4237              |
| $R^2$       | 0.9808            | 0.9835              |

3.3. Adsorption kinetic studies
The adsorption kinetics of ACT onto TACC 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, ($R^2 = 0.9950$) compared to pseudo-first-order ($R^2 = 0.4053$). Moreover, the adsorption capacity calculated ($q_{e, cal}$) value agree with the experimental data ($q_{e, exp}$). The result approved that adsorption is well described by the pseudo-second-order kinetic model. It means the chemisorption involves in the interaction between ACT and activated carbon [27].

3.4. Thermodynamic studies
Through the effect of temperature adsorption thermodynamic can be determined by varies temperature (303, 313, 323, 333 and 343 K). The Gibb’s energy ($\Delta G^0$), enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) were the parameters for thermodynamic studies were determined through equation (13) to (16). The results were showed ($\Delta S^0 = 137.65$ kJ/mol.K) and ($\Delta H^0 = 24759.92$ J/mol). The values of $\Delta G^0$ (-16947, -18323.5, -19699.9, -21076.4 and -22452.9 kJ/mol) were more towards negativity as temperature rises which were 303, 313, 323, 333 and 343 K respectively. According to the negative values of $\Delta G^0$, $\Delta S^0$ and $\Delta H^0$, it is proven that the process is spontaneous and exothermic. The results are comparable with other researcher [26].
Table 5. Pseudo-first-order, pseudo-second-order constants and $R^2$ values for adsorption of ACT on TACC at 30°C

| Initial dye concentration (mg/L) | $q_{e_{exp}}$ (mg/g) | Pseudo-first-order model | Pseudo-second-order model |
|---------------------------------|----------------------|--------------------------|---------------------------|
|                                 | $q_{e_{cal}}$ (mg/g) | $K$ (1/min) | $R^2$ | $q_{e_{cal}}$ (mg/g) | $K_2$ (1/min) | $R^2$ |
| 25                              | 15.1356              | 11.3370 | 0.0101 | 0.7092 | 17.3910 | 0.0575 | 0.9693 |
| 50                              | 30.3959              | 7.9287  | 0.0106 | 0.4053 | 32.5733 | 0.0017 | 0.9950 |
| 75                              | 35.4314              | 19.0327 | 0.0106 | 0.8698 | 38.7597 | 0.0009 | 0.9896 |
| 100                             | 36.6151              | 18.6251 | 0.0117 | 0.7452 | 39.3701 | 0.0011 | 0.9930 |

4. Conclusion
As a conclusion, it was proven that TACC is adsorbing ACT with 33.3 mg/g of adsorption capacity. The equilibrium studies, adsorption kinetic and thermodynamic studies were examined using vary initial concentrations and temperatures. As a result, it showed that the Freundlich model is best fitted for this adsorption of ACT onto TACC through correlation coefficient ($R^2 = 0.9183$) with supported by smallest error analysis. The Freundlich model is associated with heterogeneous and multilayer surface formation. Moreover, kinetic studies showed pseudo-second-order is well presented the adsorption process. Thermodynamic studies were found that Gibbs energy, $\Delta G^0$ is more negativity as all temperature rises from 303 to 343 K, while both $\Delta H^0$ and $\Delta S^0$ were also negative value. This reflects that process is spontaneous and exothermic. The innovative approach in this research study, by introducing the TACC as a medium for the adsorption process is relevant for research nowadays.

Acknowledgment
The authors would like to acknowledge the Bridging Grant Universiti Sains Malaysia (304/PJKIMIA/6316498) for financial support for this research work.

Reference
[1] Barnes K K, Kolpin D W, Furlong E T, Zauag D S, Meyer M T and Barber L B 2008
[2] Yacob H, Ling Y E, Hee-young K, Zainura O, Noor Z, Fadhill M, Din M, Mat S and Hun L T 2017 173 165–73
[3] Price O R, Hughes G O, Roche N L and Mason P J 2010 6 677–84
[4] Agency E M 2016 44 1–77
[5] Agency E M 2018 44 1–48
[6] Boxall A B A, Rudd M A, Brooks B W, Caldwell D J, Choi K, Hickmann S, Innes E, Ostapyk K, Staveley J P, Verslycke T, Ankley G T and Beazley K F 2012 120 1221–9
[7] Arsson D G O L 2009 P 28 2522–7
[8] States U 2018 How PPCPs Enter the Environment 1–6
[9] Division E H 2014 Acetaminophen in Drinking Water
[10] Patneedi C B and Prasadu K D 2015 Rasayan J. 8 2008–11
[11] Lishman S, Smyth S A, Sarafin K, Kleywegt S, Toito J, Peart T, Lee B, Servos M, Beland M and Seto P 2006 Sci. Total Environ. 367 544–58
[12] Verlicchi P, Aukidy M Al and Zambello E 2012 Sci. Total Environ. 429 123–55
[13] PubChem 2018 Acetaminophen 1–116
[14] States U, Medicines E, States U, Paracetamol P, Patent F P, Other A, Pregnancy O, Mechanism C, Chemical P C, Ahfs S R and License M M 2018 Paracetamol 01
[15] Nawi M A and Zain S M 2012 Appl. Surf. Sci. 258 6148–57
[16] Bahrudin N N and Nawi M A 2017 React. Kinet. Mech. Catal. 124 153–69
[17] Carabineiro S A C, Thavorn-amornsri T, Pereira M F R, Serp P and Figueiredo J L 2012
Catal. Today 186 29–34
[18] Tonucci M C, Gurgel L V A and Aquino S F de 2015 Ind. Crops Prod. 74 111–21
[19] Freundlich Herbert 1907 Über die Adsorption in Lösungen Zeitschrift für Phys. Chemie 57U 385
[20] Khamanur T, Tg A, Zamri M, Sakinah M, Munaim A and Abdul Z 2017 Int. Res. J. Eng. Technol. 4 2–6
[21] Ghaffari H R, Pasalari H, Tajvar A, Dindarloo K, BakGoudarzi B, Alipour V and Ghanbarnejad A 2017 Int. J. Eng. Sci. 6 1–11
[22] Senusi F and Abd. Karim K 2011 Colloq. Humanit. Sci. Eng. CHUSER 2011 37–42
[23] Ho Y.S. 2004 Citation Review of Lagergren Kinetic Rate Equation on Adsorption Reactions Scientometrics 59 171–7
[24] Ho Y S and McKay G 1999 Pseudo-second order model for sorption processes Process Biochem. 34 451–65
[25] Mohd N, Fadhil M, Ery A, Fauziah S and Draman S 2015 Isotherm and thermodynamic study of paracetamol removal in aqueous solution by activated carbon 10 9516–20
[26] Rey-mafull C A, Tacoronte J E, Garcia R, Tobella J, Llópiz J C and Iglesias A 2014 Comparative study of the adsorption of acetaminophen on activated carbons in simulated gastric fluid 1–12
[27] Ferreira R C, Lima H H C De, Cândido A A, Junior O M C, Arroyo P A and Carvalho K Q De 2015 Adsorption of Paracetamol Using Activated Carbon of Dende and Babassu Coconut Mesocarp 9 717–22