Batch adsorption studies for ketoprofen removal via *Dillenia Indica* peel activated carbon

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Abstract. Removal of ketoprofen using *Dillenia Indica* peel activated carbon was investigated using batch adsorption at a laboratory scale. Chemical activation method with the aid of phosphoric acid was utilised in preparing the activated carbon. The adsorption experiments were evaluated using various factors which are initial concentration, adsorbent dosage, and pH of ketoprofen. The optimum condition was determined to be at pH 6 and adsorbent dosage of 0.4 g with a most KTP uptake of 8.354 mg/g. The experimental findings showed that adsorption is favorable at lower pH. Isotherm studies were conducted and the data indicated that Langmuir isotherm was well fitted to the adsorption process and the pseudo-second-order model was more preferable in simulating the kinetic process. In essence, *Dillenia Indica* peel activated carbon was proven as being a favourable adsorbent for the uptake of ketoprofen in batch mode.

1. Introduction

These days, organic pollutants have raised concerns worldwide as these pollutants are expected to have negative environmental impacts. Examples of organic pollutants are pharmaceuticals, surfactants, dyes and pesticides [1]. These compounds are adversely found in the water environment as these substances are intensively used in daily life. These chemicals make significant contributions primarily because of the release of untreated wastewater as well as human consumption. As humans consumed the pharmaceutical products, the compounds that do not being absorbed by the body were excreted and flushed together in form of urine or feces. These contaminants will flow to the sewage system and subsequently make their way through nearby water sources and posing threat to the end-user of water [2].

The improper handling and disposal of these substances have contributed to various problems in the aquatic environment including human health. The structure of the substances that contain different functional groups has made it difficult to degrade and cause facile bioaccumulation [3]. Owing to their toxicity, organic pollutant remains in the environment, will pollute and disrupted the food chain of the living organism.
One of the common organic pollutants that usually detected on the surface of the water is ketoprofen (KTP), which is derived from pharmaceutical contaminants. KTP is a member of non-steroidal anti-inflammatory drugs (NSAIDs) classes. This drug is commonly used in relieving pain and stiffness caused by rheumatic disorder [4]. It is extensively used by the elderly which commonly suffered various types of rheumatic pains. Although their benefit in relieving pains, the presence of a large amount of the drug and higher consumption have led to the occurrence of the drug on the surface of the water. A trace of drugs including KTP have been found on the surface of the water in the Asian country. KTP was found to be the highest occurrence among the other drugs in the Taiwanese River which is in the concentration of 110 to 620 ng/L [5]. While in Algeria, KTP has been detected in the drinking water with a concentration up to 273 ng/L [6].

A present study found that the exposure of KTP toward the zebrafish had caused risk in their growth including the embryonic and the early-stage growth of the zebrafish [7]. This shows that KTP can be used as an indicator for pharmaceutical toxicity as this drug has a significant impact on the enzymatic activity and biological tissues of aquatic organisms. Even though these medications were detected in low doses, it is crucial to remember the time of exposure as well as the sensitivity of a population. Anti-inflammatory medications can cause gastrointestinal disturbances and kidney damage when exposed for an extended time [8].

In order to control the occurrence of the contaminants, several methods have been discovered by researchers such as ozonation [9], adsorption [10] and advanced oxidation [11]. Among all the methods found, adsorption is more preferred due to its advantages in simplicity in operation and low-cost consumption. This technique have been used widely in eliminating various contaminants in water and wastewaters such as dyes, organic and inorganic substances, and heavy metals. Batch adsorption is often practices in adsorbing contaminants from a liquid solutions in a small amount.

By performing adsorption method, the adsorbent comprised of activated carbon was usually utilized in eliminating pollutants from wastewaters. Several precursor were utilized in the synthesis of activated carbon. The uses of wood and coal in producing the activated carbon can contributed to a high cost due to the limited sources in certain developing countries. Thus, an agricultural by products or industrial wastes were discovered in producing a promising activated carbon for adsorption process. Besides, the usage of these materials as the precursor can help to reduce the accumulation of wastes. Some of example of biomass or waste residues that were utilized are coconut shell [12], sesame husk [13], and tea waste [14]. In this research, an activated carbon has been produced from Dillenia Indica peels by chemical activation method. This activation method comprises two steps which are impregnation and carbonization [15]. The phosphoric acid was used as the dehydrating agent.

The primary goal of this investigation is to evaluate the performance of activated carbon prepared by chemical activation methods in adsorbing KTP and evaluate the effect of each parameter used. The adsorption kinetics and isotherms were evaluated to determine the behavior on adsorption of KTP.

2. Methodology

2.1. Materials
Ketoprofen (KTP) which was used in the research as the adsorbate was purchased from Alfa Aesar (United Kingdom). Sodium hydroxide and hydrochloric acid were obtained from HmbG and Fisher Scientific, respectively. 95% denatured ethanol used in preparing the stock solution for KTP was obtained from HmbG. Phosphoric acid (85%) and sodium chloride were acquired from Merck which were used as an activating agent in preparing activated carbon and for analysis of pHpzc, respectively. Analytical-grade chemicals were used throughout the research.

2.2. Production of adsorbent
The Dillenia Indica fruits that have been collected were cleaned with distilled water and cut into smaller parts to obtain the peels. The peels were then dried under the sun for 2 days and were ground into smaller pieces. The process continued with the impregnation method. This method utilized phosphoric acid
(H$_3$PO$_4$) as the activating agent and also act as the dehydrating agent [16]. A ratio of 2:1 (dry weight of acid: dry weight of raw materials) was used to impregnated the raw material at room condition for 24 h [16]. After complete with the impregnation, the sample was oven-dried with temperature of 90 °C for 12 h and subsequently carbonized with a flow of nitrogen gas. The carbonization process was performed at 500 °C with a contact time of 2 h. Then, the carbonized sample was left at ambient condition until completely reach neutral temperature. The sample was washed with a basic (0.1 M NaOH) and an acid (0.1 M HCl) solution until reaching pH of 6 or 7. The sample then was oven-dried at 90 °C for 12 h before can be used as an adsorbent.

2.3. Adsorption experiments
Batch adsorption experiment of KTP was performed at a laboratory scale with different operating parameters. KTP was dissolved in 10% ethanol to create a stock solution. The poor solubility of KTP in water allows ethanol to be employed as a solvent and solubilizing agent [17]. The experiments were performed in 250 mL conical flask and the mixture of activated carbon and KTP solutions at different dosage and concentration were shake using an orbital shaker at 130 rpm. The temperature was maintain at room temperature. The shaking process were continued until an equilibrium removal was achieved. At different time interval, a small amount of solution was extracted from the conical flask to be analyse for it concentration using Shimadzu UV-1800 Spectrophotometer, Japan. The sample solution was filtered using nylon syringe filter to ensure the sample is clean from unwanted particle that can alter the final concentration of the sample. The wavelength to determine the concentration of KTP is 260 nm. The percent removal and amount of KTP adsorbed at equilibrium can be obtained using the formula:

$$\text{Percent removal, } % = \frac{C_o - C_e}{C_e} \times 100$$

$$q_e = \frac{(C_o - C_e) \times V}{m}$$

where $C_o$ and $C_e$ are the concentration of KTP at initial condition and stable state (mg/L), respectively. $m$ and $V$ are the mass of the activated carbon (g) and amount of solution (L).

Various parameters which are pH, concentration of adsorbate and adsorbent dosage were carried out to analyse the outcome of each parameter on the adsorption process. Kinetics and isotherms studies for the removal of KTP were evaluated based on the data obtained from the experiments.

3. Findings and analysis

3.1. The effect of adsorbent dose
Figure 1 shows a plot of different amount of adsorbents at varying time versus the uptake of KTP. The elimination of KTP was investigated at various amount of activated carbon ranging from 0.2 to 1.0 g at 30 °C with a constant shaking speed of 130 rpm. 60 mg/L of KTP solution and 480 min of contact time were kept unchanged throughout the experiments. It was expected a decrease in the amount of KTP uptake when the adsorbent dosage was increased to 1.0 g. Agglomeration of the activated carbon occurred when the amount of adsorbent dosage is high had cause decreased the surface area for adsorption to take placed. The optimum amount of adsorbent required for the removal is achieved at 0.4 g. Besides, as the number of active sites exceeds the amount of adsorbate available, the surface on adsorbent will achieve an equilibrium state and will reduced the amount KTP adsorbed [18]. Available binding sites will be unsaturated by KTP molecules [19]. Smaller changes in terms of KTP adsorbed can be observed when the adsorbent dose increased beyond 0.4 g.
3.2. The influence of pH

A pH range from pH 2 to 12 were investigated at a constant initial concentration of KTP, temperature and adsorbent dosage. The pH value was adjusted using NaOH and HCl to achieve the desired pH. Figure 2 depicts a plot of adsorption power versus pH for KTP adsorption. Based on the plot, it shows that the adsorption potential declined from 4.917 to 3.247 mg/g as the pH value rose from pH 2 to 12. The adsorption process is favorable at lower pH compared to a higher pH value. Approaching higher pH, adsorption capacity is lower may due to the competitiveness of OH ions. Using the pH drift method, the pHpzc for the adsorbent was achieved at pH 5.0 and the pKa value for KTP is 4.45. When the pH is less than 5.0, the surface of activated carbon has a positive charge and acquired negative charged as the pH rise. While, at pH lower than 4.45, KTP is in unionized form as the value of pKa is 4.45 and it carries a negative charge as the pH rise above 4.45. The hydrophobic interaction between the solution of KTP and activated carbon is one of the interaction that can be utilised to describe the adsorption mechanism at various pH levels. As the pH value higher than the pKa value for KTP and lower than pHpzc, the electrostatic force was expected to occur, when there is an interaction between the negative and positive charge of activated carbon. Thus, the adsorption is favorable around pH 4. At higher pH, an electrostatic repulsion occurred as the activated carbon get negatively charge and interact with the negative charge solution [20].
3.3. The influence of initial concentration of KTP

The influence of various initial concentrations was determined by studying the concentration of KTP between 20 to 100 mg/L. The mass of activated carbon and temperature were kept constant at 0.4 g and 30 °C, respectively. The plot of different initial concentrations versus adsorption capacity at a respective time can be in figure 2. An increased in concentration from 20 to 100 mg/L had caused an increased in the adsorption capacity from 2.456 to 5.997 mg/g. The relation between the adsorbate and the adsorbent can be enhanced as the concentration increases and thus increase the amount of KTP adsorbed [21]. Based on the plot, it is observed that when the KTP concentration was greater than 60 mg/L, the value of \( q_e \) does not show large differences between them. This is because, the adsorption sites were filled with the adsorbate when a higher concentration is applied [18]. The amount of KTP adsorbed at the first minutes of adsorption process for the different concentrations increased rapidly until 150 min for 20 and 40 mg/L and started slowed down until equilibrium condition is achieved. The presence of a large number of accessible sites for adsorption is thought to enhance KTP absorption and as the adsorption continued, the active sites become saturated with adsorbate and reached equilibrium.

![Figure 2](image2.png)

**Figure 2.** Effect of different concentrations of KTP.

3.4. Adsorption isotherm

The isotherms that were used in analysing the adsorption behaviour of KTP are Langmuir and Freundlich isotherm. Langmuir. Isotherms studies are important in determining the interaction between adsorbent and adsorbate.

The Langmuir isotherm is often utilized to characterize adsorbate monolayer adsorption on activated carbon. The isotherm equation is as follows [22]:

\[
q_e = q_m \frac{K_L C_e}{1 + K_L C_e}
\]

where \( q_m \) is the maximum uptake of adsorbate (mg/L) and \( K_L \) is the constant for Langmuir model (L/mg). \( C_e \) and \( q_e \) are the equilibrium concentration and adsorption potential (mg/L), respectively. The linear equation for Langmuir isotherm after been rearrange is given by:

![Figure 3](image3.png)

**Figure 3.** Effect of different concentrations of KTP.
The Freundlich isotherm, on the other hand, is employed to describe multilayer adsorption. Freundlich isotherm's linear equation is as follows:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \( n \) is the uptake intensity and \( K_F \) is the Freundlich isotherm constant (mg/g)(L/mg)^{1/n}, respectively. The sorption process heterogeneity is described by the value of \( 1/n \) [23].

Table 1 and figure 4 below show the adsorption isotherm parameter for the two isotherms and isotherms plots for Langmuir isotherms, respectively. Based on the table, the uptake of KTP throughout the analysis follows Langmuir isotherm as the correlation coefficient value, \( R^2 \) is the highest compared to Freundlich isotherm. This indicates that the adsorption behaves as monolayer sorption where the process occurred only on the activated carbon's surface [24]. The \( R_L \) value obtained from was utilised to depict the nature of adsorption whether the adsorption is favorable, unfavorable or linear [25]. Based on the value obtained, it shows that the value of \( R_L > 0 \) indicates favorable adsorption. The highest uptake of KTP determined by the Langmuir isotherm is 8.354 mg/g. While the Langmuir constant for adsorption energy is 0.037 L/mg. The \( K_L \) value for the process is not very large indicates that the adsorption occurred normally [24].

Freundlich isotherm has a lower \( R^2 \) value than Langmuir isotherm and this makes Freundlich less suitable in describing the adsorption of KTP. The value of \( 1/n \) is 0.499. As the value of \( 1/n \) is smaller, the more heterogeneous the adsorption process. A range of values between 0.1 to 0.5 shows that the adsorption occurred easily compared to when the value reached 2.0 [25]. A high value for \( K_F \) reflects that there is a high affinity of KTP toward the activated carbon.

### Table 1. The adsorption isotherm parameters for adsorption of KTP.

| Isotherms | Parameters          | Value  |
|-----------|---------------------|--------|
| Langmuir  | \( R^2 \)           | 0.994  |
|           | \( q_m \) (mg/g)    | 8.354  |
|           | \( K_L \) (L/mg)    | 0.037  |
|           | \( R_L \)           | 0.212-0.574 |
| Freundlich| \( R^2 \)           | 0.968  |
|           | \( K_F \) (mg/g)(L/mg)^{1/n} | 0.759  |
|           | \( 1/n \)           | 0.499  |
3.5. Adsorption kinetics

The rate of solute released to the adsorbent at a specific condition was analyzed using kinetic models. The most common models used are pseudo-first-order and pseudo-second-order models.

The pseudo-first-order model, sometimes recognized as the Langergen model, is the most general model for describing adsorption rate using adsorption capacity. The linearized form for both of the models are as follows [26]:

\[
\ln (q_e - q_t) = \ln q_e - k_1 t \\
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + k_1 t
\]

where \(k_1\) is the rate constant for the pseudo-first-order model (1/min) and can be deduced from the plot's gradient. While the second order rate constant is denoted as \(k_2\) (g/mg.min). \(q_t\) and \(q_e\) are the quantity of KTP uptake at any time \(t\) and balance condition (mg/L), respectively.

The results of the studies were matched with the two kinetic models and the output shows that the adsorption is well fitted with the pseudo-second-order model. Figure 4 depicts the model's linear plot. The correlation coefficient values for different concentrations for this model are reaching 1.0 \((R^2 > 0.9)\). Table 2 shows the adsorption kinetic parameters for the two kinetic models. Based on table 2, the value of calculated \(q_e\) for the second-order model depicted small differences against value obtained in adsorption experiment, \(q_e\) exp. This reinforces the idea that the model of pseudo-second-order is ideal for the uptake of KTP. Due to the large KTP distribution on the adsorbent surface, the adsorption rate was greater at low concentration. When compared with the pseudo-first-order model, the value of rate constant and \(R^2\) for this model are much smaller. Thus, the pseudo-second-order model has a desirable adsorption kinetic and believe to follow the chemisorption process [27].

Table 2. The kinetic parameters for the adsorption of KTP.

| Initial NPX concentration (mg/L) | \(q_e\), exp (mg/g) | \(q_e\), cal (mg/g) | \(k_1\) (1/min) | \(R^2\) | \(q_e\), cal (mg/g) | \(k_2\) (g/mg.min) | \(R^2\) |
|----------------------------------|---------------------|--------------------|----------------|--------|---------------------|-------------------|--------|
| 20                               | 2.4568              | 1.470              | 0.0068         | 0.9326 | 2.5641              | 0.0100           | 0.9923 |
| 40                               | 4.1005              | 2.3092             | 0.0069         | 0.9111 | 4.2974              | 0.0064           | 0.9949 |
| 60                               | 5.2728              | 3.3241             | 0.0073         | 0.8735 | 5.6370              | 0.0039           | 0.9912 |
Figure 5. Pseudo-second-order model for adsorption of KTP at different concentrations.

4. Conclusions
Activated carbon produce from low-cost activated carbon was successfully produce by chemical activation method. The adsorption of ketoprofen (KTP) was conducted at laboratory scale under batch experiment. The peel of *Dillenia Indica* fruit was utilized to produce a low-cost activated carbon. Different parameters or conditions which are adsorbent dosage, initial adsorbate concentration and pH of solution were used to utilise in analysing the removal of KTP. The activated carbon was successfully produced using H₃PO₄ as the activating agent with an adsorption capacity of 8.354 mg/g. According to the adsorption isotherm, the mechanism is well adapted with the Langmuir isotherm model. Furthermore, the pseudo-second-order model suits the adsorption kinetics well, revealing that the process has a high adsorption rate.

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