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Chemically Treated Chicken Bone Waste as an Efficient Adsorbent for Removal of Acetaminophen

Nurshuhada Amira Yusoff, Norzita Ngadi*, Hajar Alias, Mazura Jusoh

Department of Chemical Engineering, Faculty of Chemical Engineering, University Teknologi Malaysia, 81310 UTM Johor Bahru, Johor
norzita@cheme.utm.my

Present of pharmaceutical as the emerging pollutants arise the concerns of environment community regarding the potential impact of acetaminophen (ACT) on ecological and human health. Adsorption process has been proven as an effective treatment being activated carbon as the adsorbent to remove many types of pollutant including low concentration of pollutants. However, on large scale industrial processes, utilisation of activated carbon is limited because of their high production cost. Synthesis of waste materials as a precursor of adsorbent is an attractive approach in sustainable management and economic availability. In this study, the removal of ACT from aqueous solution by chemically treated chicken bone (AC) waste was investigated. The adsorption process was conducted in a batch adsorption and affected by several experimental parameters including contact time, pH, adsorbent dose, initial concentration and temperature. With AC dosage of 0.1 g about 93 % of 1,000 mg/L ACT was removed from the aqueous solution that had pH of 2 and temperature of 25 °C. Kinetic of ACT adsorption was well described by pseudo-second order kinetic model. Meanwhile, effect of initial concentration of acetaminophen adsorption data was fitted well with Freundlich isotherm model with an R^2 of 0.9909. Finally, the data obtained from effect of temperature was used to determine the adsorption thermodynamic including the enthalpy, ΔH, Gibbs energy, ΔG and entropy, ΔS. It was found that the ΔG was negative at all temperature while both, ΔH and ΔS was also negative between temperatures of 25 °C to 70 °C indicating the process of ACT adsorption was exothermic reaction and the adsorption reaction is spontaneous at low temperature.

1. Introduction

In recent decades, present of pharmaceutical in the environment have being a concern among the environment community and scientist. Pharmaceuticals have been labelled as new emerging environment pollutants as they are recently found in increasing amount all around the world (García-Mateos et al., 2015). In last decades, production of pharmaceutical compounds have rapidly increased as the increasing of human population; hence, it is not surprising that high number of used prescription drugs have been detected in the aquatic environment due to their important role in the treatment and prevention of disease in both humans and animals (Rakić et al., 2015). Presence of pharmaceutical has been detected in trace amounts as the development of high sensitivity analytical instrument with several techniques. Generally, its low concentration may not cause immediate fatal effect to humans but it may lead to dangerous impact on human health in a long term including acute and chronic damage, accumulation in tissues, reproductive damage, inhibition of cell proliferation and behavioural changes (Wu et al., 2012).

Paracetamol is also known as acetaminophen is the most common detected pharmaceutical because it is widely used in our society as analgesic and anti-inflammatory drug which are pain-controlling and fever reducing and due to its availability and affordability (Mohd et al., 2006). Since most of the pharmaceutical products including paracetamol are not biodegradable, they are ubiquitous in the natural and easily accumulate in aquatic environment which can give adverse effect to the health of human and other living things especially marine life instead of environmental effect. Since water is an essential resource for life in all ecosystems, an effort has been made to improve the water treatment system. Adsorption process is the most preferable method by industry to remove many types of pollutant being activated carbon as the adsorbent.

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Activated carbon can be prepared from any form of organic and carbonaceous material such as animal bone (Znad and Frangeskides, 2014), palm kernel shell (Se et al., 2013), rice hull (Mukoko et al., 2015) and tea waste (Dutta et al., 2015). Its high surface area and high porous network enable to react with other heteroatoms consequently creating abundance of surface functionalities on its surface and structural (Cabrita et al., 2010). Use of animal bone as the precursor of activated carbon and its ability to remove acidic dyes (El Haddad et al., 2013) and toxic heavy metal (Cechinel and de Souza, 2014) from wastewater have been reported by several studies. In this present work, the efficiency of chicken bone derived activated carbon was evaluated in the removal of pharmaceutical residues especially paracetamol or acetaminophen from aqueous solution.

2. Methods

2.1 Preparation and characterisation of activated carbon

Chicken bone was used as the carbonaceous precursor of activated carbon. The chicken bone waste was collected from a cafeteria, Mak Ngah Catering in Universiti Teknologi Malaysia. The bones was washed with water and boiled in distilled water for an hour to remove the attached meats and fats. Then, the bones were dried in an oven at 70 °C for 24 h. The dried bone was subsequently carbonised in a furnace for an hour at 500 °C. The carbonised bone or also known as bone charcoal was crushed and sieved into powder form in the size range of 75 µm to 80 µm. Orthophosphoric acid (H_3PO_4) was used as the activation agent to prepare the activated carbon (Marsh and Reinoso, 2006). Preparation of chicken bone activated carbon was adapted from (Mukoko et al., 2015) with slight modifications. Bone charcoal was impregnated with 10 mL of 0.5 M H_3PO_4 (1:2 weight of sample / volume of acid) until the mixture form a paste. The paste was transferred into a crucible and carbonised in the furnace at 500 °C for 2 h. The chemically activated product was allowed to cool at room temperature, washed with distilled water and dried overnight at 70 °C. Surface area and textural properties of the activated carbon was analysed using adsorption/desorption of nitrogen (N_2) at 77 K.

2.2 Adsorption experiment

Adsorption experiment was conducted in batch reactor conditions by Erlenmeyer flask in order to obtain the amount of ACT remaining in the solution. In each test, 50 mL of the solution containing 1,000 mg/L of ACT was poured into the flask and 0.1 g of activated carbon was added into the solution. The suspension was then placed on the shaker and stirred at 200 rpm. The determined parameters and their ranges were as follows: contact time (5 h in equilibrium test), pH of the solution (2-11), and adsorbent dosage (0.05 - 2 g), initial ACT concentration (1,000 – 5,000 mg/L) and solution temperature (25 – 70 °C).

2.3 Analysis

Concentration of ACT remaining in the solution was determined using a spectrophotometer at 243 nm. The amount of ACT adsorbed onto AC was calculated based on percentage removal as Eq(1):

$$\text{Acetaminophen percentage removal}=\frac{(C_0\text{-}C_t)}{C_0}\times 100 \qquad (1)$$

where C_0 and C_t are concentration of ACT at initial time and time t of the contact time (mg/L) while V and m represent as the volume of ACT solution and mass of the adsorbent added.

Duplicate tests were conducted to ensure the reproducibility of the results and the average of these two measurements represents the result for each test. Adsorption study was performed to determine the mechanism of adsorption kinetic, adsorption isotherm and adsorption thermodynamic.

3. Result and discussion

3.1 Characterization of Activated Carbon

Figure 1 shows the nitrogen adsorption-desorption isotherm of the chemically activated carbon. The result observes that the AC samples have type III isotherm which explains the formation of multilayer adsorbate on the AC samples. Formation of multilayer can be explained by the strong interaction of adsorbate with an adsorbed layer (Leddy, 2012). The S_{BET} surface area of AC was 80.586 m^2/g and the total pore volume of AC was 0.297 cm^3/g. Figure 2 depicts the pore size distribution of AC. According to Barret-Joyner-Halenda (BJH) method, the average pore diameter of AC was 172.272 Å. As shown in Figure 2, the peak was observed in the region between 20 Å to 500 Å which indicating the AC structure was mesopores. Theoretically, pore diameter of less than 20 Å showed the structure of micropores material while pore diameter of more than 500 Å showed the structure of mesopores material.

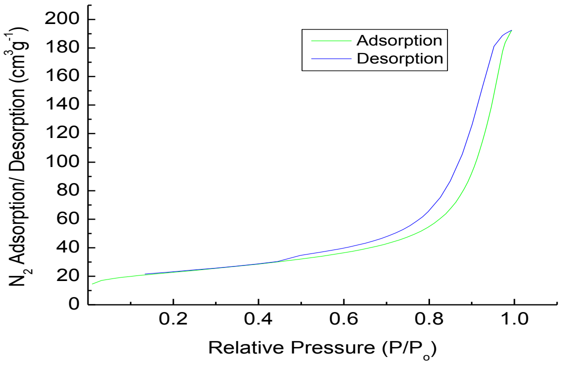

Figure 1: N_2 adsorption- desorption isotherm at 77 K

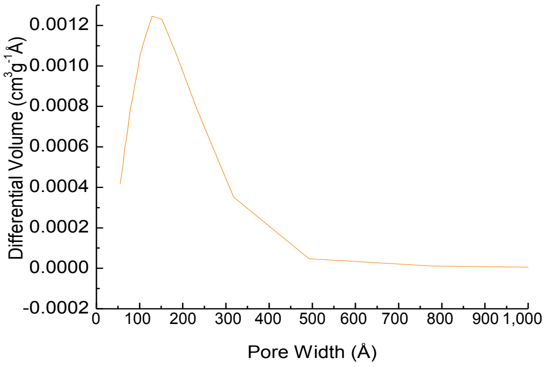

Figure 2: Pore size distribution

3.2 Effect of contact time on adsorption

Study of contact time in adsorption process was conducted to determine the equilibrium time required by the AC to adsorb the highest concentration of the ACT. Figure 3 shows the result of ACT adsorption by the effect of contact time. The experiment was conducted by varying the contact time starting from 60 to 300 min. The trend showed that the adsorption rate of ACT was increased rapidly at initial contact time until the equilibrium adsorption was approached at 120 min. Since the equilibrium phase was achieved, further increase in contact time did not show any significant change in the adsorption rate of ACT.

3.3 Effect of pH solution on adsorption

Figure 4 shows the result of adsorption of ACT onto activated carbon by the effect of pH of the solution. Adsorption of ACT affected by pH solution was conducted in different range of pH values starting from pH 2 to pH 11. The adsorption rate of ACT onto chicken bone derived activated carbon tends to be high in acidic solution. The amount of ACT removed was high at pH 2 with almost 93.4 % of the initial concentration of ACT. This phenomenon can be justified by considering the neutral charge of ACT molecules which are adsorbed by the equally neutral and positively charged adsorbent surface (Ferreira et al., 2015). At pH 12, adsorption rate of ACT onto the activated carbon was the lowest due to the repulsion of ACT molecules by negatively charged carbon surface; hence, it can be concluded that adsorption process can be affected by the pH solution by considering the change of adsorbent surface charge distribution which are consequently varying the adsorption rate according to the adsorbate functional group (Grassi et al., 2012).

3.4 Effect of adsorbent dosage

Effect of adsorbent dose in batch equilibrium studies is one of the important parameter because it is indicating the sorbent-sorbate equilibrium of a system as well as the adsorbent's adsorption capacity (Mukoko et al., 2015). The effect of adsorbent dose was studied using three different masses of adsorbent which was 0.05 g, 0.1 g and 0.2 g. Figure 5 shows the percentage removal of ACT with respect to the adsorbent dosage. It was observed that the adsorption rate of ACT was directly proportional to the mass of adsorbent used. Increasing in ACT removal can be justified by considering the availability of more sorbent surface or more active sites for ACT adsorption resulting from increasing of the adsorbent dosage (Ismail and AbdelKareem, 2015).

3.5 Effect of initial concentration on adsorption

Figure 6 shows the percentage removal of ACT from aqueous solution at different initial concentration. The result observed that increasing in initial concentration of ACT resulted in a decrease in percentage removal of ACT due less vacant sites on the adsorbent for the adsorption. At low concentration, adsorption rate of ACT was high because the availability of vacant sites on the activated carbon was exceeding the amount of ACT molecules in solution. Similar result was observed in the previous research on the adsorption of ACT by rice hull activated carbon (Mukoko et al., 2015)

3.6 Effect of temperature on adsorption

Temperature is another important parameter affecting the adsorption process. Adsorption reaction are normally exothermic reaction which illustrates an increase in adsorption capacity with decreasing temperature (Grassi et al., 2012). As illustrate in Figure 7, percentage removal of acetaminophen decrease as the temperature increases, which indicates that the adsorption reaction of acetaminophen was exothermic reaction. The adsorption of acetaminophen was high at room temperature with 93 % of acetaminophen was removed from the initial concentration. A previous study showed that acetaminophen adsorption decreases with increasing temperature may due to the fact that the physical bonding between the adsorbate molecules and active sites of carbon surface weakened in high temperature which reducing the adsorption of acetaminophen (Dutta et al., 2015).

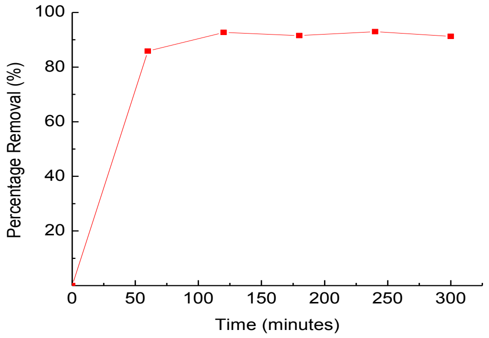

Figure 3: Effect of contact time on ACT adsorption

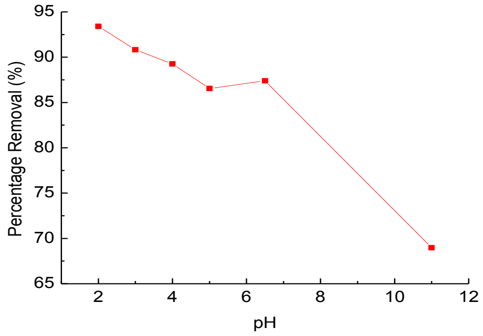

Figure 4: Effect of pH on ACT adsorption

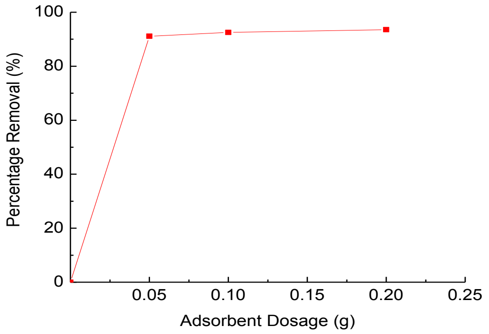

Figure 5: Effect of adsorbent dosage on ACT adsorption

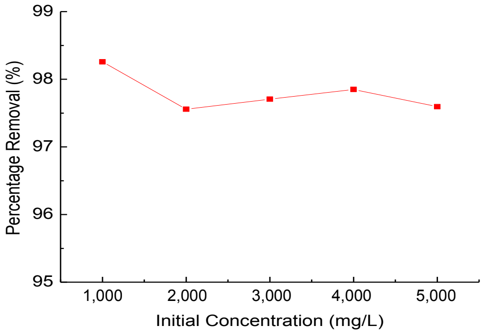

Figure 6: Effect of initial concentration on ACT adsorption

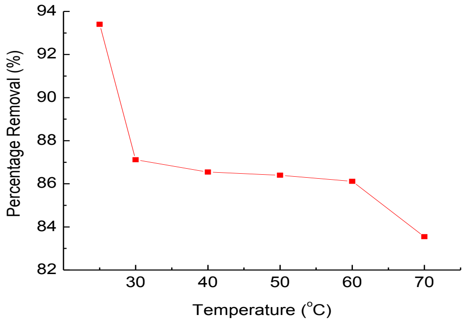

Figure 7: Effect of temperature on ACT adsorption

3.7 Adsorption kinetic

Adsorption rate of adsorbate onto adsorbent can be determined by several kinetic models including pseudo first order, pseudo second order and intra-particle diffusion (Mukoko et al., 2015). Table 1 shows the kinetic details of ACT adsorption onto chicken bone derived activated carbon. Kinetic study of ACT adsorption was studied by measuring the change of ACT concentration with respect to the contact time of adsorption process. The results illustrate that adsorption of ACT obeys the pseudo-second order model with R2 value of 0.9996 which indicate that the coefficient of determination is favourable and the experimental data can be adjusted to the model. Fitness of the experimental data to the pseudo-second order explains that the ACT adsorption is likely to be controlled by chemisorption. Moreover, similar result was obtained in previous research on adsorption of ACT using activated carbon treated with NH_4Cl (Mashayekh-Salehi and Moussavi, 2016). Intra-particle diffusion is not seem as the rate limiting step because the line of best fit does not through the origin which indicate intra-particle diffusion is not the main adsorption mechanism (Znad and Frangeskides, 2014).

Table 1: Kinetic details of ACT adsorption

Kinetic model	Pseudo-first order	Pseudo-second order	Intra-particle diffusion
Equation	$\ln(q_e-q)=\ln q_e-\left(\frac{k_1}{2.303}\right)t$	$\frac{t}{q}=\frac{1}{k_2 q_e^2}+\left(\frac{1}{q_e}\right)t$	$q=k_p t^{\frac{1}{2}}+C_i$
Constant	k_1=0.012 min^{-1} q_e= 13.171 mg g^{-1}	k_2=8.963 × 10^{-4} g mg^{-1} min^{-1} q_e=465.116 mg g^{-1}	k_p=2.634 mg g^{-1} min^{-2} C_i=420.071 mg g^{-1}
R^2	-0.35015	0.9996	0.68381

3.8 Adsorption Isotherm

Langmuir and Freundlich isotherms are the most commonly used isotherms to describe the adsorption. Table 2 shows the isotherm details of ACT adsorption onto activated carbon with respect to initial concentration. Adsorption data of ACT was well described by Freundlich isotherm models with the correlation coefficient of R^2 value of 0.9909 compared to 0.64434 for Langmuir isotherm. Application of Freundlich isotherm to the equilibrium data of ACT indicated the multilayer coverage of chicken bone activated carbon by ACT molecules.

Table 2: Isotherm details for ACT adsorption

Isotherm model	Langmuir	Freundlich
Equation	$\frac{C_e}{q_e}=\frac{1}{q_{max}}+\frac{C_e}{q_{max}}$	$\log q_e=\log k_F+\frac{1}{n}\log C_e$
Constant	q_{max}=10,188.134 mg/L k_L=390.099	n=1.74 k_F=40.726
R^2	0.64434	0.9909

3.9 Adsorption Thermodynamic

The thermodynamic data is required to reflect the feasibility and favorability of the adsorption (El Haddad et al., 2013). The parameters involve including free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) are determined by the change of the equilibrium constant with respect to the temperature Straight line of ln k_D (k_D = q_e/C_e) against 1/T was plotted according to Eq(2) and the calculated thermodynamic parameters were presented in Table 3.

$$\ln k_D=-\frac{\Delta H}{RT}+\frac{\Delta S}{RT} \tag{2}$$

Table 3: Parameter of adsorption thermodynamic for ACT removal

Temperature (K)	Free Energy,(kJ/mol) $\Delta G = -RT\ln k_D$	Enthalpy Change, (J/mol)	ΔHEntropy Change, ΔS (J/mol K)
298	-4.850	-13.208	-30.993
303	-3.069		
313	-3.040		
323	-3.105		
333	-3.134		
343	-2.657		

In this study, ΔG values were negative for all range of temperature which indicated the reaction was energetically favourable at low temperature. As shown in Table 3, the value of ΔH is negative and it proves that the adsorption of ACT is an exothermic reaction which explains the decreasing of ACT adsorption with increasing in temperature. Negative value of ΔS indicates that no significant change on entropy when the temperature is increased as similar in the previous research on adsorption of ACT using carbon activated with NH_4Cl (Mashayekh-Salehi and Moussavi, 2016).

4. Conclusion

Chicken bone derived activated carbon was used as adsorbent in adsorption study to remove acetaminophen (ACT) from aqueous solution. The results observed that 120 min of contact time was required to adsorb approximately 93 % of ACT using 0.1 g activated carbon at pH solution of 2 and the initial concentration of 1,000 mg/L with temperature of 25 °C. The adsorption kinetic was found to obey the pseudo-second order with respect to the contact time while the adsorption data was fitted to the Freundlich isotherm equation at various initial concentrations. The removal efficiency of ACT was found to increase resulting from decreasing the temperature which explained the exothermic nature of the adsorption process. In conclusion, the study found that, chicken bone waste derived activated carbon was potentially used as adsorbent for removal of pharmaceutical waste.

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