ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

ISOTHERM AND THERMODYNAMIC STUDY OF PARACETAMOL REMOVAL IN AQUEOUS SOLUTION BY ACTIVATED CARBON

Norzila Mohd, Muhammad Fadhil Aiman Ery Sudirman and Sarifah Fauziah Syed Draman
Universiti Teknologi MARA, Bukit Besi Campus, Dungun, Terengganu, Malaysia
E-Mail: norzi085@tganu.uitm.edu.my

ABSTRACT

Paracetamol is a pain reliever and fever reducing drug used widely in Malaysia. Since paracetamol is a pharmaceutical product it is not biodegradable, hence it will not decompose easily. This will pose an environmental and health problem as the residue will seep into wastewater and groundwater supply and eventually in drinking water. An experiment was set up to investigate the performance of activated carbon and modified cellulose for adsorption of paracetamol from aqueous solution by batch method. The effect of pH and temperature was chosen as a parameter in this experiment. The removal percentage was increased at higher temperature and decreased at a basic solution for both adsorbent. Then, the data were fitted to Langmuir, Freundlich and Temkin adsorption isotherm. It was found out that the effect of pH adsorption equilibrium data was fitted well with the Langmuir model with an R^2 of 0.9522. Adsorption of thermodynamic was carried out by using the data from effect of temperature and was found out that the ΔG at all temperatures was negative, ΔH and ΔS was positive. Therefore, the process was spontaneous and favorable at high temperature.

Keywords: adsorbent, pharmaceutical waste, isotherm, thermodynamics.

INTRODUCTION

Paracetamol is also known as acetaminophen is a mild analgesic used as a pain reliever and fever reducer. Paracetamol widely and commonly used in Malaysia due to its availability and affordability. However, like many other pharmaceutical products, there is an amount of dose taken could not be adsorbed by the body, therefore they can enter the environment via excretion from the sewage system. Usually, unused or expired Paracetamol is thrown away, thus creating an environmental problem as it enters to groundwater supplies. Many pharmaceutical products are not biodegradable, the residue can be found in treated water and even drinking water [1].

Since the pharmaceutical product is not biodegradable, the consequences may be dreadful as it can affect not just environmental but also health and life of human and other organisms especially marine life as it can seep into open water like rivers and lakes. A conventional method like sewage treatment in which it uses physical, chemical and biological method fail to eliminate or degrade the majority of these compounds and they are partially removed; henceforth leaving residue accumulates in drinking water supplies [2]. In spite of that, these micropollutants detections have been improved in recent years. In [3] reported majority of these micropollutants detected are in low concentration; ranging from a gram to nanogram per liter. Nonetheless, these residues still present and as time pass by it will accumulate slowly and pose unintended long-term effect.

According to [4], advanced technologies like ozonation, reverse osmosis and membrane filtration can assure the adsorption and removal of paracetamol and pharmaceuticals from drinking water. Since acetaminophen is an organic compound, ozonation process is useful in removing it by infusing water with ozone to facilitate organic breakdown. Reverse osmosis and membrane filtration can effectively separate water from paracetamol as the membrane are selectively blocking it from entering water to the other side because of its size. The major drawbacks of this process are that it is too expensive and to install it in every waste water treatment facility in near impossible. Activated carbon or also known by many names such as activated charcoal or activated coal is a processed carbon which derived from organic material with high carbon content such as wood and coal. The main characteristic of activated carbon is that it has high microporosity thus increase its surface area for adsorption and chemical reactions. In addition, due to this advantage it is used as filtration and purification process. In this study, commercial activated carbon was chosen as an adsorbent. This is due to its large surface area, availability in the laboratory, affordability and its quality as small amount of activated carbon is significant in adsorption.

METHODOLOGY

Materials

The material used in this experiment was commercial activated carbon and paracetamol both prepared by the lab. The activated carbon was supplied by Ever Gainful Enterprise Sdn Bhd that marketed under the label R&M Chemicals which the product name is Carbon

ARPN Journal of Engineering and Applied Sciences

(Activated Powder). Paracetamol was supplied by Acros Organics which product name is 4-acetamidophenol, 98%.

Methods

There were two parameters use in running the experiment, namely pH and temperature. Each experiment, a parameter would be manipulated variable while the other were set constant at a certain value, the experiment was duplicated. For instance, initial concentration was set to 100ppm, contact time was 120 minutes, adsorbent dosage would be 1g/L and agitation speed was 150rpm.

In this experiment, pH 2 to 9 were tested. For pH 2 and 3. The paracetamol solution was prepared accordingly. The rest of the pH solution would be adjusted by using 0.1M of hydrochloric acid and sodium hydroxide. Next, 0.1 gram of activated carbon was put into each 100mL paracetamol solution. Then, the sample was put into orbital shaker with 150rpm and 2 hours contact time. After that, the sample was transferred into a centrifuge. Filtration was done and ready to be send to ultraviolet (UV)-Visible Spectrophotometer for sample reading.

The paracetamol solution with pH 3 was made. The sample was tested by using incubator shaker, so that the temperature of 25 °C until 40 °C can be controlled and adjusted. The subsequent step was similar to effect of pH.

Isotherms and thermodynamic studies

The isotherm batch experiments were carried out by using 0.1g of paracetamol, the pH of the solution at 2, 3, 4, 5, 6, 7, 8 and 9, the initial concentration of 100ppm which was constant throughout the experiment, allowing sufficient time of 120 minutes for adsorption equilibrium, so further experiment were conducted at 120 minutes contact time. Thermodynamic study of paracetamol adsorption experiments was performed which following the same procedure at 25, 30, 35 and 40 °C.

The supernatants were filtered through Advantec 110mm filter paper supplied by Toyo Roshi Kaisha, Ltd. The remaining paracetamol concentration was analyzed by using Varian Cary 50 Conc UV-Visible Spectrophotometer. All the experiments and analysis have been carried out in duplicate.

RESULTS AND DISCUSSIONS

Effect of temperature

The percentage removal of paracetamol increased with the rise of temperature as shown in Figure-1. These indicated that the process is endothermic. A study by [5] found that increased in temperature would increase mobility of adsorbent. Other studies by [6] concluded that higher temperature may also attributed with enlargement of the adsorbent pore size.

Hence, in this experiment, it can be said that the cause of increment in the removal of paracetamol at higher temperature was due to increased mobility of paracetamol and enlargement of activated carbon pore and surface. The smallest increment of removal percentage is probably due to activated carbon which has almost reached its temperature threshold. This is supported by research conducted by [7] which stated that the increase in removal is no longer obvious due to the offset of deception if the temperature exceeds the threshold.

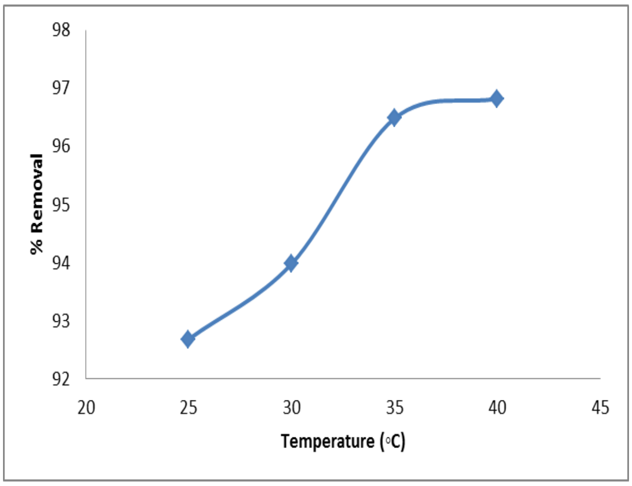

Figure-1. Percentage removal of paracetamol in various temperatures.

Effect of pH

Figure-2 presents the effect of pH to the percentage of paracetamol removal in aqueous solution. As illustrated in Figure-2, the percent removal was decreasing as the solution became more basic. The highest % removal was 92.17% at pH 2, and the lowest was 44.02% at pH 9. The loading capacities decreased at a basic solution pH, which can be linked with two factors that is the ionization of adsorbate and charges surface of activated carbon at given pH [5].

During the adsorption process, carbon surface may exist either in both positive and negative charges or contain both charges depending on its nature. At pH 9, almost 50% paracetamol molecule exists as anionic form. From the previous study, it is stated that the activated carbon surface is negatively charged. This situation explains why the removal was decreased at basic solution, the negative-negative interaction of both adsorbent and adsorbate repel each other. Adsorption at acidic pH (2-4), the negative charge of activated carbon was neutralized most of negatively charged surface with hydrochloric acid, and the paracetamol exists as neutral form. The repulsive electrostatic effect was reduced between the neutral molecule of adsorbent and positive charged activated carbon surface was greatly minimized. Therefore, this condition facilitates the increase percentage removal of paracetamol.

A similar study was conducted by [5] on the removal of ibuprofen from aqueous solution of waste derived activated carbon. The pH changes able to change

VOL. 10, NO 20, NOVEMBER, 2015 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

the dissociation of adsorbate. From the experiment ibuprofen being weak electrolyte, at pH 2 ibuprofen exist as neutral molecule, at pH 5 half anionic form and at pH 7 almost completely in anionic form. This suggested that the interaction of carbon surface with deprotonated ibuprofen is weak.

In addition, pH changes also affect the surface chemistry of the adsorbent due to the dissociation of functional groups. The carbon surface is either positively charged or negatively. As highlighted by [5], ibuprofen removal reduces at basic pH where most of ibuprofen mostly in anionic form (pH > pKa) and the surface of activated carbon is negatively charged. Hence, the negative changes surface repels the anionic ibuprofen.

Since the functional group of paracetamol and ibuprofen are similar, it can be assumed that paracetamol characteristic in adsorption is almost similar to ibuprofen even with different pKa and can be compared to the previous study [5]. As expressed by [8], phenolic drugs are 50% ionized when the pH equals with their pKa. As stated earlier, the pKa of paracetamol is 9.78 [9] or 9.5 [8]. At pH 2, paracetamol mostly exists as neutral molecule and as it approach its pKa, about 50% of paracetamol was ionized and become anionic molecule. The decrease amount of adsorption indicates that a weaker interaction of carbon surface with anionic molecule of paracetamol.

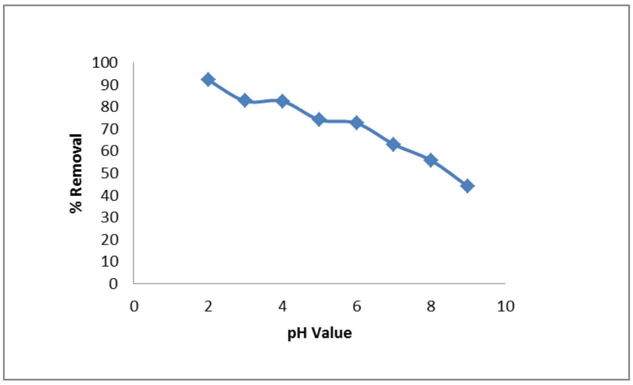

Figure-2. Percentage removal of paracetamol in various pHs.

Adsorption isotherm

Adsorption isotherm is used to illustrate the adsorbate concentration and the quantity of material adsorbed. The equation is always represented as a straight line equation. In this experiment, Langmuir model, Freundlich model and Temkin model were used to identify adsorption capacity.

Langmuir model

This model is only applicable in the cases where only one molecular layer of adsorbate is formed at the adsorbent surface [10]. Monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of the adsorbate in the plane of the surface. This model can be represented as follows:

$$\frac{Ce}{qe} = \frac{1}{(q_{max}K_L)} + \frac{1}{q_{max}}Ce \tag{1}$$

where q_{max} is the monolayer adsorption capacity of adsorbent or also can be defined as maximum adsorption (mg/g), K_L is the Langmuir adsorption constant (L/mg), C_e is concentration exit (mg/L) and q_e is adsorption at equilibrium (mg/g). However, the value for q_{max} and K_L can only be determined from the slope and intercept of the graph of C_e/q_e versus Ce (Figure-3). To calculate the value of q_e, the equation is as follows:

$$qe = \frac{(C_o \quad C_e)V}{m} \tag{2}$$

where C_o is the concentration initial (mg/L), V is volume of the sample solution (L) and m is the mass of adsorbent (g).

Freundlich model

Freundlich model proposes the heterogeneous energetic distribution of active sites, which accompanied by the interaction of adsorbed molecules [10]. The Freundlich linear equation can be seen below:

$$\text{Log } qe = \text{Log } K_F + \frac{1}{n}\text{Log } Ce \tag{3}$$

where Log K_F is constant related to adsorption capacity and 1/n is adsorption intensity. Both values can be calculated from the slope and intercept of a plot of Log q_e versus Log C_e.

Temkin model

Temkin model assumes the effect of some indirect interactions amongst adsorbate particles, and suggest a linear decrease in the heat of adsorption of all molecules in the layer [10]. The isotherm can be expressed as follows:

$$qe = a_t + 2.303 b_t \text{Log } Ce \tag{4}$$

where a_t and b_t are Temkin constant which can be obtained from the slope and intercept of Log C_e versus qe.

VOL. 10, NO 20, NOVEMBER, 2015 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

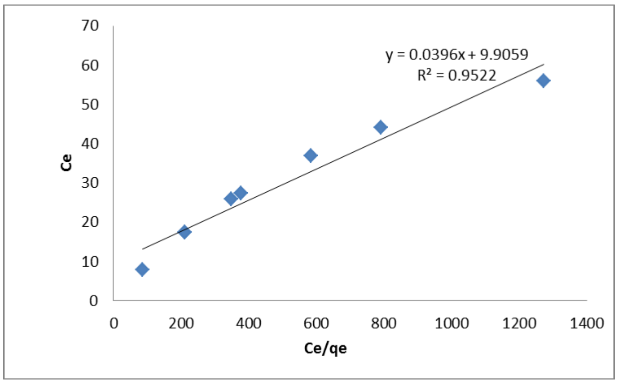

Figure-3. Graph of C_e/q_e versus Ce.

The experimental data for all three models can be as shown in Table-1.

Table-1. Adsorption parameter for all three isotherm.

Isotherm models	Adsorption parameters
Langmuir	**q_{max} = 25.253**
	K_L = 250.149
	R^2 = 0.952
Freundlich	N = -2.809
	K_F = 0.516
	R^2 = 0.846
Temkin	a_t = 0.149
	b_t = -0.024
	R^2 = 0.912

From Table-1, by comparing all three models, Langmuir isotherm is the best fitted where it coefficient correlation, R^2 is nearer to 1. Hence, the adsorption in this experiment is best defined as monolayer adsorption of paracetamol onto surface of activated carbon.

Adsorption thermodynamic

From the effect of temperature, adsorption thermodynamic can be determined by temperature ranging from 25 °C-40 °C (298K-313K). Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined by equation as follows:

$$K_D = \frac{qe}{Ce} \tag{5}$$

$$\Delta G = RT\ln K_D \tag{6}$$

$$\ln K_D = \frac{\Delta S}{R} \quad \frac{\Delta H}{RT} \tag{7}$$

It was found out that the value of ΔH was 1.6628×10^{-3}kJ/mol and ΔS was 0.0399J/mol. Based on Table-2, the value of ΔG was more towards negativity as temperature rises. As been put forward by [10], when ΔG is negative and both ΔH and ΔS are positive, the process is spontaneous and favored high temperature. In this experiment all of three values of ΔG, ΔH and ΔS were comparable with [10]. Therefore, adsorption of paracetamol onto activated carbon is spontaneous and favored high temperature. Thus, it explained about why the intake of paracetamol increases as temperature increase where the enthalpy is positive; the process uses the heat supply from surrounding to do the adsorption process.

Table-2. Values of Gibbs free energy of temperature between 298K-313K.

T (K)	ΔG (kJ/mol)
298	-23403.145
303	-24322.316
308	-26165.355
313	-26865.959

CONCLUSIONS

In conclusion, it can be seen that from the effect of temperature, the percentage of removal was increasing as the temperature increase, which was from 92.68% to 96.82%. The removal increment relates to the mobility of paracetamol and enlargement of activated carbon size at high temperature. For effect of pH, the percentage removal was decreasing as the pH became more basic. The percentage removal has decreased from 92.17% at pH 2 to 44.02% at pH 9. This is due to the weak interaction in the anionic form of paracetamol at basic pH and repulsive force of negatively charged activated carbon surface at basic pH. Out of the three isotherms, Langmuir model was best fitted with correlation coefficient (R^2) is 0.9522. Hence, the adsorption occurs when paracetamol formed a layer onto the activated carbon surface. From the result of thermodynamic studies, it was found out that the ΔG was more towards negativite as all temperature rises, meanwhile both ΔH and ΔS were positive. This means the process is spontaneous and more favorable at high temperature.

ACKNOWLEDGEMENT

The authors gratefully acknowledge Research Acculturation Grant Scheme (RAGS) 600-RMI/RAGS 5/3 (209/2014) under MOHE and Research Management Institute of Universiti Teknologi MARA for the financial support through this project.

ARPN Journal of Engineering and Applied Sciences

REFERENCES

[1] R. Baccar, M. Sarrà, J. Bouzid, M. Feki and P. Blánquez. 2012. Removal of pharmaceutical compounds by activated carbon prepared from agricultural by-product. Chemical Engineering Journal. 211-212: 310-317.

[2] I. Cabrita, B. Ruiz, A. S. Mestre, I. M. Fonseca, A. P. Carvalho and C. O. Ania. 2010. Removal of an analgesic using activated carbons prepared from urban and industrial residues. Chemical Engineering Journal. 163(3): 249-255.

[3] M. A. Kizer and M. D. Smolen. (2008). Treatment methods for removal of pharmaceuticals and hormones from drinking water. Division of Agricultural Sciences and Natural Resources, Oklahoma State University. http://dasnr22.dasnr.okstate.edu/docushare/dsweb/Get/Version-9380/BAE-1523.pdf.

[4] I. Villaescusa, N. Fiol, J. Poch, A. Bianchi and C. Bazzicalupi. 2011. Mechanism of Paracetamol removal by vegetable wastes: The contribution of л-л Interactions, hydrogen bonding and hydrophobic effect. Desalination. 270 (1-3): 135-142.

[5] S. Sikarwar and R. Jain. 2014. Kinetics and thermodynamic study of balsalazide adsorption by unsaturated polyester resin (UPR): A non carbon adsorbent. Water, Air, & Soil Pollution. 225(2): 1-10.

[6] A. S. Mestre, J. Pires, J. M. Nogueira, J. B. Parra, A. P., Carvalho and C. O. Ania. 2009. Waste-derived activated carbons for removal of ibuprofen from solution: Role of surface chemistry and pore structure. Bioresource Technology. 100(5): 1720-1726.

[7] P. Hu, Y. Zhang, F. Lv, X. Wang, F. Wei, X. Meng and S. Jiang. 2014. Organic pollution removal from TNT red water using cu-impregnated activated Coke. Water, Air, & Soil Pollution. 225 (4): 1-10.

[8] Cairns D. 2012. Physicochemical properties of drugs: Essentials of pharmaceutical chemistry. 2nd Ed. Pharmaceutical Press, London, UK. pp. 57-80.

[9] M. K. E. Al-Shwaiyat. 2013. Spectrophotometric determination of paracetamol by reduction of 18-molybdo-2 phosphate heteropoly anion. Jordan Journal of Chemistry. 8(2): 78-89.

[10] K. M. S. Surchi. 2011. Agricultural waste as low cost adsorbents for Pb removal: Kinetics, equilibrium and thermodynamics. International Journal of Chemistry. 3(3): 103-112.