

Effect of Adsorption Parameter on the Removal of Aspirin Using Tyre Waste Adsorbent

Asyiq Azman, Norzita Ngadi*, Dyg Khairunnisa Awg Zaini, Mazura Jusoh, Zurina Mohamad, Agus Arsad

School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
 norzita@cheme.utm.my

In recent years, pharmaceutical compound has been detected in small concentration in our surface and ground water. This detection raises a lot of concern as is it reported that pharmaceutical compound can bring adverse effect to the environment even at low concentration. Besides that, there is a growing fear that this compound will eventually end up in human drinking water, thus effecting human health. This prompt a lot of research on the removal method for this particular compound. Adsorption is seen as the most viable option because of its high efficiency, low cost and it is environmentally friendly. In this study, the adsorbent used is carbon black derived from tyre waste via pyrolysis at 800 °C. The carbon black was treated with 6 M of nitric acid (HNO₃) at 90 °C for 0.5 h before being subjected to thermal treatment at 600 °C for 1 h. The response of the adsorption study is the removal of aspirin. There were five adsorption parameters that were varied in this study which are the contact time (until equilibrium), initial pH of aspirin solution (pH 3, pH 7, pH 11), temperature (30, 50, 70 °C), initial concentration (10-100 mg/L) and adsorbent dosage (0.1 g, 0.5 g, 1.0 g). The best removal capacity obtained was 40.40 mg/g of aspirin at pH 3, temperature of 30 °C, 100 mg/L initial concentration and 0.02 g adsorbent dosage.

1. Introduction

Pharmaceutical compounds have recently been recognized as emerging pollutant as they have been detected in almost all compartment of the environment especially in the water system (Teo et al., 2016). This is very alarming considering that pharmaceutical compounds are known to cause adverse effect to the environment even at low concentration (Li, 2014). This is made worse by the fact that no law and regulation exist to monitor their presence in the environment (Frédéric and Yves, 2014).

Aspirin is one of the most consumed and produced pharmaceutical compound (Jones et al., 2002). As a result, aspirin is also one of the most commonly detected pharmaceutical compound in the environment. A lot of research are being done in order to find effective way to remove this type of compound. Advance treatment such as advanced oxidation processes (Broséus et al., 2009), biodegradation (Cruz-Morató et al., 2014), membrane filtration (Radjenović et al., 2008) and adsorption (Hussain et al., 2010) have shown positive results in removing this type of compound. Adsorption is seen as the most promising removal method because of its versatility in removing different pollutant and also its efficiency.

Activated carbon is the most prominent adsorbent being used. However, due to the cost of commercial activated carbon and its unrenewable origin, a lot of emphasizes have been put in making activated carbon from waste material such as spent coffee ground (Lavecchia et al., 2016), peach stones (Álvarez-Torrellas et al., 2015) and oil palm endocarp (Marrugo et al., 2015). Tyre waste is another waste material that have a potential to be used as an adsorbent because of its high carbon content called carbon black (CB) (Saleh and Danmaliki, 2016).

Table 1 shows some of the study in utilizing tyre waste as an adsorbent. This study looks to take advantage of this high carbon content of tyre waste in making an adsorbent for the removal of aspirin. In this study, the adsorbent was synthesized by subjecting the CB with chemical treatment and thermal treatment. The resulting tyre waste adsorbent (TWA) were then subjected to batch adsorption experiment where the effect of adsorption

parameter: contact time, pH, temperature, initial concentration and adsorbent dosage were investigated for the removal of aspirin.

Table 1: Studies on tyre waste as an adsorbent

Pollutant	Adsorption Capacity (mg/g)	Reference
Mercury	211.00	Manchón-Vizuete et al., 2017
Xylene	14.87	Alamo-Nole et al., 2011
Copper	1.52	Calisir et al., 2009

2. Materials and methods

2.1 Materials

CB derived from tyre waste were obtained from QCS Biotechnology SDN. BHD located at Senai, Johor. Tyre waste were subjected to pyrolysis at 800 °C to obtain the CB. Nitric acid (HNO₃) with purity of 70 % was purchased from HmbG Chemicals. 0.1 M of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust pH.

2.2 Adsorbent synthesis

The CB were first subjected to chemical treatment. 10 g of CB were impregnated with 500mL of 6 M nitric acid at 90 °C. The mixture was then shaken at 160 rpm for 1 h. Then, the CB were filtered and washed using distilled water until a neutral pH of filtrate were obtained. Next, the resulting CB were subjected to thermal treatment at 600 °C for 1 h. After thermal treatment, the resulting adsorbent were called waste tyre adsorbent (TWA) and were used for the batch adsorption experiment.

2.3 Batch adsorption experiment

The batch adsorption experiment were conducted by mixing 50 mL of aspirin solution with the specified amount of waste tyre adsorbent (TWA) and shake at 160 rpm.

The effect of contact time of aspirin adsorption was under the following condition: pH 7, 30°C, 100 mg/L of aspirin solution, 0.1 g of adsorbent and 150 min. Samples were collected from the mixture for UV-Vis analysis (300 nm wavelength) at every 10 min for the first 30 min, then every 30 min for the rest of the experiment. The optimum contact time was then selected and used for the subsequent set of experiment. The next set of experiment was conducted to study the effect of pH on aspirin adsorption by adjusting the pH of aspirin solution ranging from pH 3 to pH 11. For the effect of temperature, the experiment was conducted at 30 °C, 50 °C and 70 °C. Initial concentration of aspirin was varied from 10 mg/L to 100 mg/L to study the effect of initial concentration of aspirin. Three different adsorbent dosage (0.1 g, 0.5 g and 1.0 g) were used to study the effect of adsorbent dosage.

The amount of aspirin adsorbed to TWA at equilibrium, q_e (mg/g), was calculated using Eq(1), while aspirin adsorbed at time t , q (mg/g) was calculated using Eq(2). The percentage removal of aspirin was calculated using Eq(3).

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

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

$$\text{Removal \%} = \frac{(C_0 - C_e)}{C_0} 100 \quad (3)$$

In Eq(1), Eq(2) and Eq(3), C_0 is the initial concentration of aspirin, mg/L. C_e is the concentration of aspirin at equilibrium, mg/L. C_t is the concentration of aspirin at time t , mg/L. V is the volume of aspirin solution, L. W is the weight of adsorbent used.

3. Results and discussion

3.1 Effect of contact time

Figure 1 shows the effect of contact time on the removal of aspirin by TWA. From the figure it can be seen that the adsorption of aspirin happens at a high rate for the first 10 min where the adsorption capacity increase significantly to 20.12 mg/g. The adsorption of aspirin reached equilibrium at 60 min.

Initially, a lot of unoccupied active site were available for the adsorption of aspirin. Furthermore, the high concentration gradient of aspirin also drives the adsorption process forward. As more aspirin were adsorb on the surface of the adsorbent, both of these factors deteriorates, the concentration gradient decrease and less active site for adsorption are present. This may also due to the repulsive force between the adsorb aspirin on the surface of the adsorbent and the aspirin in the aqueous solution (Gulipalli et al., 2011). The maximum adsorption capacity when equilibrium was reached is 21.5 mg/g.

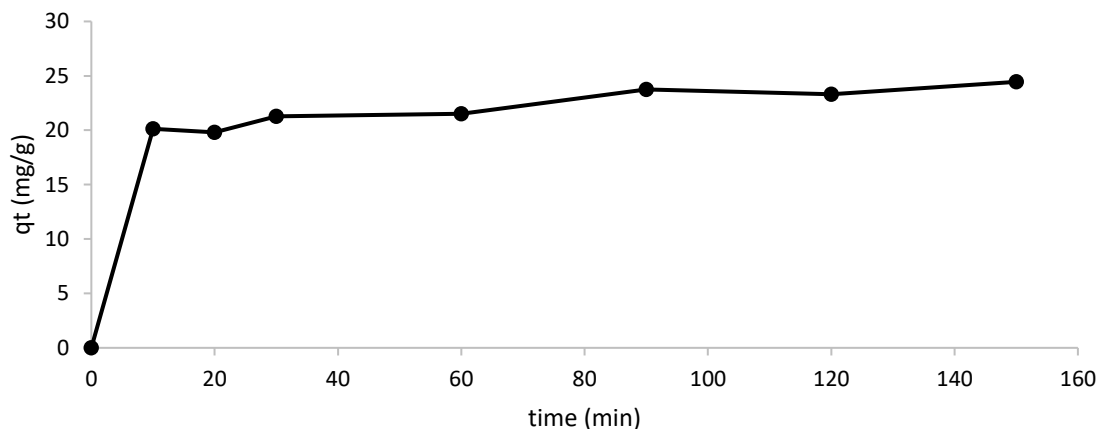


Figure 1: The effect of contact time on aspirin adsorption (pH 3, 30 °C, 100 mg/L initial aspirin solution, 0.1 g adsorbent dosage)

3.2 Effect of pH

The result for the effect of pH on the adsorption of aspirin is shown at Figure 2.

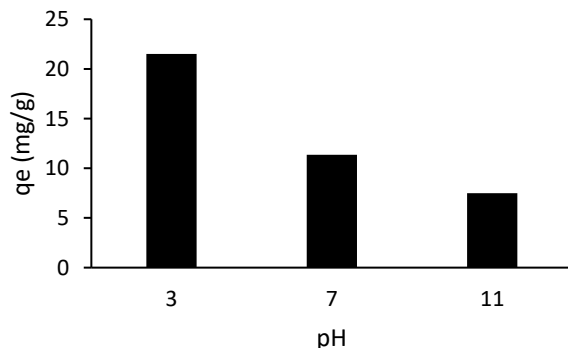


Figure 2: The effect of pH on aspirin adsorption (60 min contact time, 30 °C, 100 mg/L initial aspirin solution, 0.1 g adsorbent dosage)

The best pH for the adsorption of aspirin is pH 3 which is the initial pH of aspirin without addition of sodium hydroxide. A decrease in adsorption were observed with an increase in pH. The adsorption capacity decrease from 21.50 mg/g at pH 3, to 11.34 and 7.48 mg/g at pH 7 and 11. The same trend were obtained from previous study where the adsorption of aspirin favours a more acidic solution (Mukoko et al., 2015).

The effect of pH on adsorption can be related to the point of zero charge (pH_{pzc}) of the TWA which is 2.13. This means that at pH more than 2.13, the adsorbent surface will be negatively charged. Aspirin is a weak acid ($pK_a = 3.5$) and undergoes partial deprotonation in water to produce negatively charge ions. By increasing the pH of aspirin solution, the surface of TWA and aspirin will be negatively charged resulting in electrostatic repulsion which hindered the adsorption (Bernal et al, 2017).

The above statement is contradicting with fact that the adsorption capacity of TWA was still high at pH 3 which is higher than the pH_{pzc} .

This lead to the conclusion that electrostatic attraction between the adsorbent and adsorbate is not the sole adsorption mechanism in this study. Instead, the interaction between aspirin and the basic oxygenated group (which were added to the surface of adsorbent during the chemical and thermal treatment) on the surface of the TWA may play a more prominent role.

3.3 Effect of temperature

The data plotted in Figure 3 shows that temperature was an insignificant factor for the adsorption of aspirin onto TWA. Very small deviation were observed even at a much elevated temperature. The adsorption capacity at temperature 30 °C, 50 °C and 70 °C were 21.50 mg/g, 22.12 mg/g and 21.45 mg/g. The same pattern had been observed before by Wong et al. (2017).

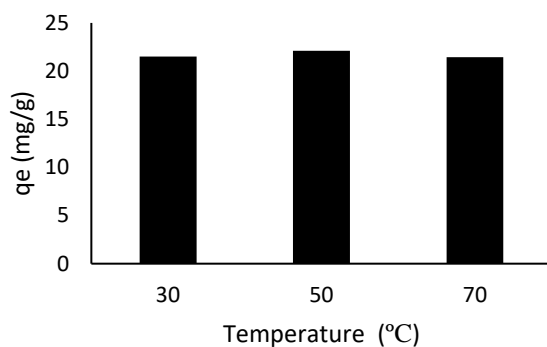


Figure 3: The effect of temperature on aspirin adsorption (60 min contact time, pH 3, 100 mg/L initial aspirin solution, 0.1 g adsorbent dosage)

This result shows that the adsorption of aspirin onto TWA occurs via chemisorption. Chemisorption is not dependent on the temperature as the bond created between the adsorbate and adsorbent need a high energy to be overcome and broken (Febrianto et al., 2009). This is in agreement with the mechanism proposed in section 3.2 in which the aspirin react chemically with the basic functional group on the TWA.

3.4 Effect of initial concentration

Figure 4 shows that by increasing the initial concentration of aspirin, the adsorption capacity increase. The increase is very significant from 4.44 mg/g at 20 ppm concentration up to 21.50 mg/g at 100 ppm which is an increase of approximately 200 %.

The mass transfer driving force between the adsorbent and adsorbate plays a significant role in this trend. A higher initial concentration will create a higher driving force because of the concentration gradient of the adsorbate (Nasuha et al., 2010). This will in turn resulted in a higher number of effective collisions of adsorbent and adsorbate thus increasing the adsorption capacity (Wong et al., 2018). After 60 mg/L of initial aspirin concentration, the percentage removal of aspirin decreases. This is because of the saturation on the surface of adsorbent.

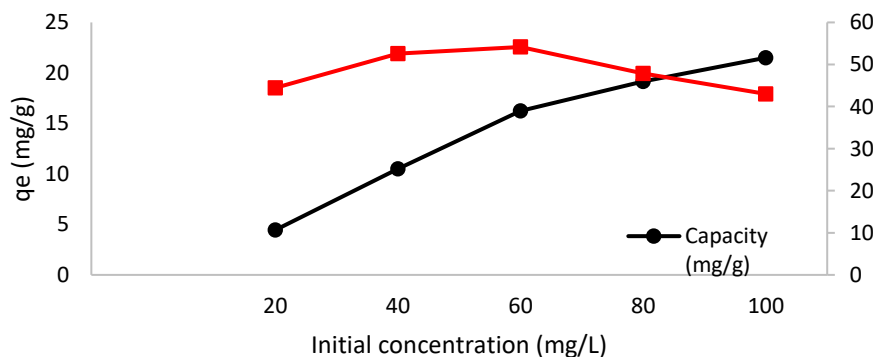


Figure 4: The effect of initial concentration on aspirin adsorption (60 min contact time, pH 3, 30 °C, 0.1 g adsorbent dosage)

3.5 Effect of adsorbent dosage

A clear trend can be seen for the effect of adsorbent dosage in Figure 5. As expected, by increasing the amount of adsorbent, the removal of aspirin increased as well. An opposing trend were observed for adsorption capacity. The adsorption capacity decrease as more adsorbent were used. The highest adsorption capacity in this study, which is 40.40 mg/g, were recorded when 0.02 g of adsorbate was used. In comparison, a study that uses carbon nanotube crosslinked with β -cyclodextrin manages to obtain an adsorption capacity of 101 mg/g (Mphahlele et al., 2017).

By increasing the adsorbent dosage, more active site for adsorption were available. This explains the trend where an increase in adsorbent dosage resulted in more removal of aspirin. As for the decreasing adsorption capacity, this is probably because some of the active sites were left unoccupied since the ratio between the adsorbate and adsorbent active site were very large (Reddy et al., 2016).

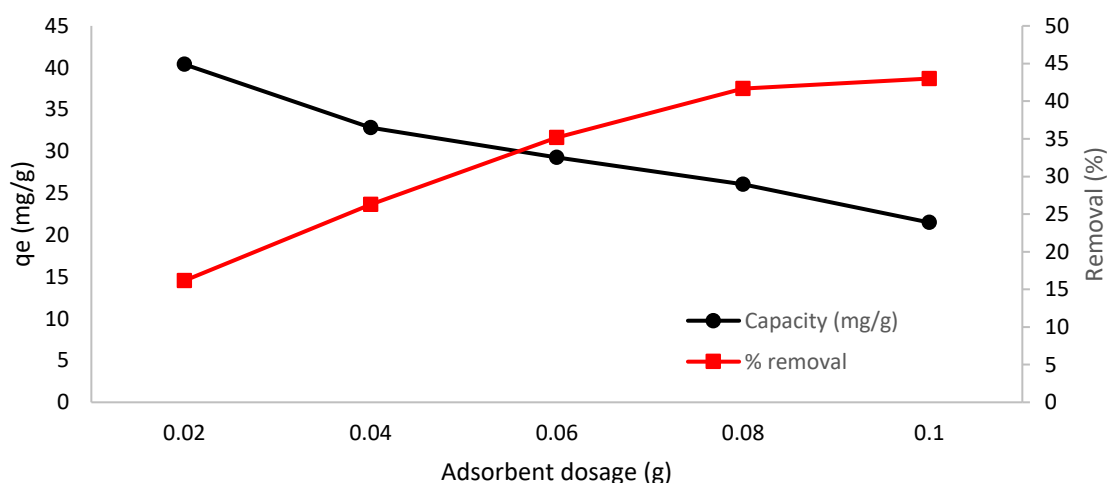


Figure 5: The effect of initial concentration on aspirin adsorption (60 min contact time, pH 3, 30 °C, 100 mg/L initial aspirin concentration)

4. Conclusion

In this study, tyre waste adsorbent (TWA) was synthesized by using both chemical and heat treatment on the tyre waste. The batch adsorption experiment shows a promising result in which the highest adsorption capacity of aspirin obtained was 40.40 mg/g at 60 min contact time, pH 3, temperature 30 °C, 100 mg/L initial aspirin concentration and 0.02 g adsorbent dosage.

References

- Alamo-Nole L.A., Perales-Perez O., Roman-Velazquez F.R., 2011, Sorption study of toluene and xylene in aqueous solutions by recycled tires crumb rubber, *Journal of hazardous materials*, 185, 107-111.
- Alvarez-Torrellas S., Garcia-Lovera R., Rodríguez A., Garcia J., 2015, Removal of methylene blue by adsorption on mesoporous carbon from peach stones, *Chemical Engineering Transactions*, 43, 1963-1968.
- Bernal V., Erto A., Giraldo L., Moreno-Piraján J.C., 2017, Effect of solution pH on the adsorption of paracetamol on chemically modified activated carbons, *Molecules*, 22(7), 1032.
- Broséus R., Vincent S., Aboufadi K., Daneshvar A., Sauvé S., Barbeau B., Prévost M., 2009, Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment, *Water research*, 43, 4707-4717.
- Cruz-Morató C., Lucas D., Llorca M., Rodríguez-Mozaz S., Gorga M., Petrovic M., Barceló D., Vicent T., Sarrà M., Marco-Urrea E., 2014, Hospital wastewater treatment by fungal bioreactor: removal efficiency for pharmaceuticals and endocrine disruptor compounds, *Science of the Total Environment*, 493, 365-376.
- Febrianto J., Kosasih A. N., Sunarso J., Ju Y.H., Indraswati N., Ismadji S., 2009, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies, *Journal of hazardous materials*, 162(2-3), 616-645.
- Frédéric O., Yves P., 2014, Pharmaceuticals in hospital wastewater: their ecotoxicity and contribution to the environmental hazard of the effluent, *Chemosphere*, 115, 31-39.

- Gulipalli C. S., Prasad B., Wasewar K. L., 2011, Batch study, equilibrium and kinetics of adsorption of selenium using rice husk ash (RHA), *J. Eng. Sci. Technol*, 6(5), 586-605.
- Hussain K., Bukhari N.I., Danish M., Hassan S.S., Tanveer M., 2010, Adsorption of paracetamol on activated charcoal in the presence of dextropropoxyphene hydrochloride, N-acetylcysteine and sorbitol, *Latino Americano Journal of Pharmacy*, 29, 883-888.
- Jones O.A.H., Voulvoulis N., Lester, J.N., 2002, Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. *Water research*, 36(20), 5013-5022.
- Lavecchia R., Medici F., Patterer S., Zuurro A., 2016, Lead removal from water by adsorption on spent coffee grounds, *Chemical Engineering Transactions*, 47, 295-300.
- Li W.C., 2014, Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil, *Environmental Pollution*, 187, 193-201.
- Manchón-Vizuete E., Macías-García A., Gisbert A.N., Fernández-González C., Gómez-Serrano V., 2005, Adsorption of mercury by carbonaceous adsorbents prepared from rubber of tyre wastes, *Journal of hazardous materials*, 119, 231-238.
- Marrugo G., Silgado K., Puello J., 2015, Adsorption of Cr (VI) by activated carbon from oil palm endocarp: adsorption isotherm and kinetic analysis, *Chemical Engineering Transactions*, 43, 613-618.
- Mphahlele K., Onyango M. S., Mhlanga S. D., 2015, Adsorption of aspirin and paracetamol from aqueous solution using Fe/N-CNT/ β -cyclodextrin nanocomposites synthesized via a benign microwave assisted method, *Journal of Environmental Chemical Engineering*, 3, 2619-2630.
- Mukoko T., Mupa M., Guyo U., Dziike F., 2015, Preparation of Rice Hull Activated Carbon for the Removal of Selected Pharmaceutical Waste Compounds in Hospital Effluent, *J Environ Anal Toxicol* S7: 008, DOI: 10.4172/2161-0525.S7-008.
- Nasuha N., Hameed B.H., Din A.T.M., 2010, Rejected tea as a potential low-cost adsorbent for the removal of methylene blue, *Journal of hazardous materials*, 175(1-3), 126-132.
- Radjenović J., Petrović M., Ventura F., Barceló D., 2008, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, *Water Research*, 42, 3601-3610.
- Reddy P.M.K., Verma P., Subrahmanyam, C., 2016, Bio-waste derived adsorbent material for methylene blue adsorption, *Journal of the Taiwan Institute of Chemical Engineers*, 58, 500-508.
- Saleh T.A., Danmaliki G. I., 2016, Influence of acidic and basic treatments of activated carbon derived from waste rubber tires on adsorptive desulfurization of thiophenes, *Journal of the Taiwan Institute of Chemical Engineers*, 60, 460-468.
- Teo H.T., Siah W.R., Yuliati L., 2016, Enhanced adsorption of acetylsalicylic acid over hydrothermally synthesized iron oxide-mesoporous silica MCM-41 composites, *Journal of the Taiwan Institute of Chemical Engineers*, 65, 591-598.
- Wong S., Lee Y., Ngadi N., Inuwa I. M., Mohamed, N. B., 2018, Synthesis of activated carbon from spent tea leaves for aspirin removal, *Chinese Journal of Chemical Engineering*, 26(5), 1003-1011.
- Wong S., Yac'cob N.A.N., Ngadi N., Hassan O., Inuwa I. M., 2018, From pollutant to solution of wastewater pollution: Synthesis of activated carbon from textile sludge for dye adsorption, *Chinese Journal of Chemical Engineering*, 26, 870-878.