

Activated Carbon Cryogel as a Potential Adsorbent for Removal of Aspirin

Mohd Asmadi^{a,*}, Nor Aishah Saidina Amin^a, Muzakkir Mohammad Zainol^a, Marfiah Ab Wahid^b, Sureena Abdullah^c, Wai Mun Khor^a

^aChemical Reaction Engineering Group (CREG), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor Darul Takzim, Malaysia

^bFaculty of Civil Engineering, Universiti Teknologi Mara Shah Alam, 40450 Selangor, Malaysia

^cFaculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia
 mohdasmadi@utm.my

Pharmaceutical substances are urged to be removed from wastewater as the pollutants bring adverse effects to both humans and the environment. Among the pharmaceutical substances, aspirin is selected as the targeted pharmaceutical waste due to its extremely high consumption. Aspirin is widely used in the world and is produced about 35,000 t/y. Carbon cryogel was chosen as the potential adsorbent to remove aspirin from wastewater, and it was synthesized from urea and furfural before activation with H₃PO₄. The effects of experimental parameters on aspirin adsorption such as pH, contact time, initial concentration, adsorbent dosage, and temperature were investigated. A maximum of 30 % of percentage removal and 30 mg/g of adsorption capacity were achieved at an initial concentration of 60 mg/L, pH 6, and 0.05 g of adsorbent at room temperature after 45 min of contact time. The activated carbon cryogel synthesized in this study is useful for application in wastewater treatment and sanitation of water

1. Introduction

Pharmaceutical wastes are among the wastewater pollutants that are required to be removed, as their presence in the water stream brings adverse effects to both human and the environment. This situation creates a concern about pharmaceutical waste disposal in the rivers in Malaysia, which may contain various types of pharmaceuticals that need to be removed. Different countries and areas dispose of different concentrations of pharmaceutical wastes. Some pharmaceutical wastes that are commonly found are acetaminophen (Yang et al., 2018), erythromycin (Hossain et al., 2018), bisphenol A (Muhamad et al., 2016), and aspirin (Azman et al., 2019). Among all the pharmaceutical wastes detected, aspirin is chosen as the target component for removal due to its high consumption. The amount of aspirin tablets used is estimated to be around 100 billion, due to its medical properties (Prado et al., 2017). Aspirin also contains the highest acute toxicity as a type of anti-inflammatory drug (Tomul et al., 2019). In some countries, aspirin can be sold without any prescription, and this contributes to the rise in the usage of aspirin and generation of pharmaceutical waste (Prado et al., 2017).

Chegeni et al. (2020) summarized the methods used for removal of drug pollutants from wastewaters, which include membrane and carbon nanotube, electrochemical processes, electrocoagulation (EC), UV/H₂O₂/oxygen systems, and adsorption. Adsorption has shown good performance as an efficient and economical method. The adsorbent plays an important role as the adsorption performance depends on the adsorbent's properties and the parameters. Previous works have reported the adsorption capacity of aspirin using activated carbon derived from spent tea leaves with 178.57 mg/g (Wong et al., 2018), graphene nanoplatelets (GNPs) with 12.98 mg/g (Ouafsi et al., 2019), and tire waste adsorbent (TWA) with 40.40 mg/g (Azman et al., 2019). Carbonaceous materials are commonly used in adsorption studies for various contaminants (Yang et al., 2019), and activated carbon is widely used in removal of different types of pollutants from water due to its sorption characteristics and properties (Tran et al., 2017). There are many types of carbon material and carbon cryogel is a potential adsorbent material. Carbon cryogel is synthesized

from various sources and has interesting properties as an adsorbent and material for other applications. Carbon cryogel has shown its advantages due to its high surface area and good porosity, which can be controlled during the synthesis and drying process. The activation process conducted on carbon cryogel is aimed to improve the surface properties.

The objective of this study is to synthesize carbon cryogel from urea and furfural and further activate it to produce an adsorbent for the adsorption of aspirin. The effects of experimental parameters on aspirin adsorption such as pH, contact time, initial aspirin concentration, adsorbent dosage, and temperature were investigated using activated carbon cryogel (ACC) to obtain the maximum adsorption capacity for aspirin removal. The adsorption performance of aspirin was observed to examine the potential of ACC as adsorbent.

2. Experimental

2.1 Material and chemicals

Urea and aspirin were purchased from Sigma-Aldrich, USA, and furfural and phosphoric acid (H_3PO_4) were purchased Merck, Germany. Ethanol ($\text{C}_2\text{H}_6\text{O}$, 95 %), sulfuric acid (H_2SO_4 , 95–97 %), zinc chloride (ZnCl_2), and potassium carbonate (K_2CO_3) were purchased from QR&C, New Zealand. Urea, furfural, H_2SO_4 , H_3PO_4 , ZnCl_2 , and K_2CO_3 were utilized to prepare activated carbon cryogel while aspirin was used to prepare a stock solution for adsorption study. All chemicals were used as received.

2.2 Synthesis of activated carbon cryogel (ACC)

Carbon cryogel (CC) precursor was synthesized according to the work of Zainol et al. (2020). Urea and furfural were used as feedstocks, and the reaction was conducted inside a Schott bottle. Distilled water was added to the mixture to dilute and homogenize the sample. The sample was stirred for 15 min for complete mixing of the sample before adding H_2SO_4 . Then, the dark brown oligomer was transferred into a Petri dish and further freeze-dried with Labfreez® freeze dryer at $-60\text{ }^\circ\text{C}$ for 3 h to form cryogel. Finally, the sample was calcined inside a furnace at $500\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ for 2 h to prepare carbon cryogel. Three ACC samples were prepared by using three different activating agents, which are H_3PO_4 , ZnCl_2 , and K_2CO_3 . Each activating agent was added into the carbon cryogel with a mass ratio of 1:1. The carbon cryogels were then activated with the chemicals at $80\text{ }^\circ\text{C}$ for 2 h. The ACCs were further calcined in a furnace at $500\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ for 1 h. The CC and ACC were characterized by using Fourier-transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET), and field-emission scanning electron microscope (FESEM) to study the surface properties and morphology.

2.3 Adsorption of aspirin from aqueous solution

Aspirin stock solution with an initial concentration of 100 mg/L was prepared by dissolving 0.1 g of aspirin in ethanol and distilled water with a volume ratio of 9:11. A screening experiment was conducted by mixing 0.1 g of ACC in 50 mL aspirin solution (100 mg/L) with different pH (2 and 6) at room temperature. The best ACC was selected based on the result of percentage removal and adsorption capacity (q_e), which were calculated by using Eq(1) and Eq(2) (Tang et al., 2017). The ACC with the highest adsorption capacity was chosen as the adsorbent for further adsorption experiments.

$$\text{Percentage removal (\%)} = \frac{(C_o - C_f)}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_f) \times V}{m} \quad (2)$$

where C_o (mg/L) is the initial concentration of aspirin, C_f (mg/L) is the final concentration of aspirin, V (L) is the total volume of the solution, and m (g) is the dosage of adsorbent.

The effect of pH was investigated by mixing 0.1 g of ACC with 50 mL of aspirin solution (100 mg/L) at room temperature. The solutions were adjusted to selected pH from 2 to 10 by using HCl and NaOH. Then, the mixtures were shaken at 200 rpm for 1 h. The optimum pH was selected based on the adsorption capacity calculated and used for the next effect study. The pH at zero point of charge (pH_{zpc}) was measured by using 0.01 mol/L of NaCl which was adjusted in a range of pH, from 2 to 12. The pH of the solution was adjusted using 0.1 mol/L HCl and 0.1 mol/L NaOH. ACC (0.1 g) was added to 50 mL of NaCl solution, and the mixture was left for 48 h. The final pH was recorded at the end of the test. The graph of final pH versus initial pH was plotted, and the point of intersection between the $y = x$ plot represents pH_{zpc} for ACC (Zainol et al., 2017). The pH_{zpc} was around pH 6. The experiment for the effect of contact time on adsorption of aspirin was conducted for 2 h with a time interval of 15 min. The effect of initial concentration of aspirin solution (40 mg/L to 100 mg/L) was investigated for adsorption study. After that, the effect of ACC dosage was investigated by altering

the adsorbent amount from 0.05 to 1 g, while the effect of temperature was investigated at room temperature, 50 °C, and 70 °C. The solution was analyzed using a UV-1280 Multipurpose UV–Visible Spectrophotometer at 226 nm, where the initial and the equilibrium concentrations of the aspirin were determined from the plotted calibration curve.

3. Results and discussion

The ACC samples synthesized from different activating agents were screened as different agents have different effects on the adsorbent's properties. The activating agents affect the adsorbent's surface morphology and chemistry, and influences adsorption performance (Wong et al., 2018). From the screening result (Figure 1), H_3PO_4 was chosen as the activating agent as the adsorption capacity for removal of aspirin was the highest at pH 2 and 6 with a adsorption capacity of 1.9 and 5.6 mg/g. The other activating agents showed only small differences in the adsorption performance. Further studies on the adsorption parameter were conducted to determine the best condition for the removal of aspirin using the selected ACC.

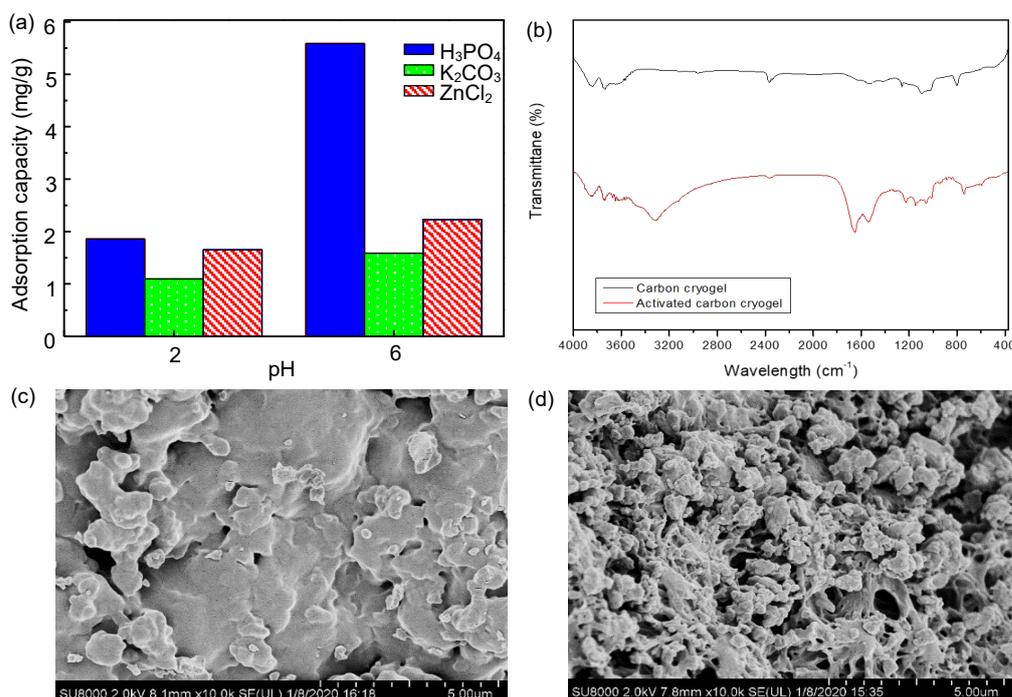


Figure 1: (a) Comparison of adsorption capacity of ACC synthesized from different activating agents, (b) FTIR spectra of CC and ACC, and morphology of (c) CC and (d) ACC via FESEM images (at $\times 10.0\text{k}$, 2 kV)

The FTIR spectra (Figure 1b) show that related functional groups or chemical bonds exist in the CC and ACC structures. The ACC sample shows clear peaks compared to CC, which is affected by the activation process that exposed more surface for analysis and provided high peak intensity. The peak observed at 3325 cm^{-1} corresponds to N–H stretching of urea in the structure. Another sharp peak at 1651 cm^{-1} represents the C=O stretching of amide and C=C bonding in the carbon structure. The frequency of 1096 cm^{-1} represents the presence of carbonyl group (C–O) in the activated carbon cryogel. The FESEM images (Figure 1c–d) show that the ACC surface consists of more pores compared to CC, which will enhance the adsorption performance. The activation process improves the surface structure of the CC by providing large surface area for the adsorption process. This is supported by the result of the surface area analysis after activation process. The CC precursor originally had a surface area of $149.0\text{ m}^2/\text{g}$, and it increased to $300\text{ m}^2/\text{g}$ after the activation process using H_3PO_4 . The adsorption of aspirin by ACC is possibly influenced by the high surface area and the existence of oxygenated groups on the surface for interaction via hydrogen bonding and electrostatic attraction.

3.1 Effect of pH on removal of aspirin from aqueous solution

Figure 2a shows that the percentage of removal and adsorption capacity increased with pH. The pH value of 6 was chosen as the selected value for subsequent parameter study as there was only a slight difference in the adsorption capacity between pH 6 and 10. The selected pH 6 is supported by the result of pH_{zpc} that was

determined in the preliminary study. A similar result was obtained by a previous work that obtained high percentage removal of around 60 % at high pH value of 8 (Chegeni et al., 2020). The adsorption of aspirin using ACC shows that the adsorbent tends to be more negatively charged at high pH (above pH 6) and causes low electrostatic attraction between aspirin anion and adsorbent. The results present small changes of aspirin molecules at high pH, showing that the electrostatic repulsive force between the adsorbent and adsorbate is not significant. The molecules possibly interact via hydrogen bonding, which is stronger than electrostatic force at high pH condition.

3.2 Effect of initial concentration on removal of aspirin from aqueous solution

Figure 2b shows the effect of initial concentration on the removal of aspirin. The percentage removal decreased when initial aspirin concentration increased. The percentage removal decrease is due to the saturation of adsorbate on the adsorbent surface. The adsorption capacity increased as the initial concentration increased from 40 to 60 mg/L. Then, the adsorption capacity decreased as the initial concentration of aspirin was further increased. This situation shows that the high initial concentration creates a higher driving force for adsorption, which increases the adsorption capacity. High concentration of adsorbate provides effective collisions with adsorbent, which increases the adsorption capacity (Wong et al., 2018). The optimum capacity is when the process has achieved saturation limit on the surfaces of the adsorbent (Zaini et al., 2019). High aspirin concentration could cause a distraction for effective collisions between the adsorbent and adsorbate and reduces the adsorption on the adsorbent. The initial concentration of 60 mg/L was selected for further parameter study due to its highest adsorption capacity.

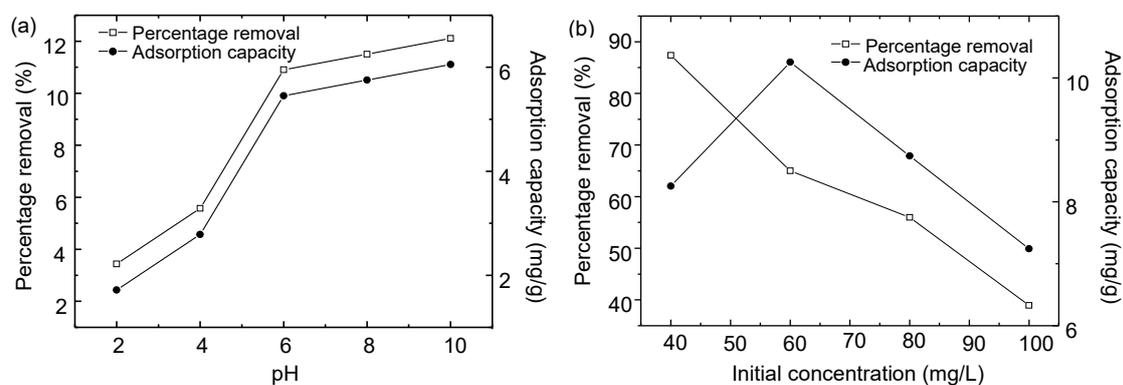


Figure 2: Effect of (a) pH (100 mg/L aspirin, 0.1 g ACC, 60 min, room temp.) and (b) contact time on removal of aspirin (pH 6, 0.1 g ACC, 60 min, room temp.)

3.3 Effect of contact time on removal of aspirin from aqueous solution

The effect of contact time on removal of aspirin is shown in Figure 3a. High adsorption rate was observed at the first 15 min, and the adsorption capacity slowly increased until it reached equilibrium at 45 min. Rapid and high adsorption rate at the initial stage is due to many vacant sites on the surfaces of adsorbent. At equilibrium, the pores of the adsorbent have been filled by the molecules of the adsorbate (Hoppen et al., 2019). Similarly, it was stated that the aspirin molecules occupying the vacant sites have caused the adsorption process to reach an equilibrium (Zaini et al., 2019). The adsorption capacity slightly decreased after 60 min of adsorption, which is possibly due to small desorption of aspirin.

3.4 Effect of adsorbent dosage on removal of aspirin from aqueous solution

Figure 3b shows the effect of adsorbent dosage on the removal of aspirin. Increasing the amount of adsorbent provides more available vacant sites for the adsorption of aspirin molecules. This increases the percentage of aspirin removal or efficiency. The inverse response was shown by the adsorption capacity of aspirin on ACC. The percentage removal was higher at a dosage of 0.5 g but it attained a low adsorption capacity. ACC dosage of 0.05 g showed the highest adsorption capacity with low percentage removal compared to other dosages. The percentage removal for all samples with different dosages have shown small variation. The selection was made by considering the highest adsorption capacity, which was the dosage of 0.05 g. Higher percentage removal could be achieved by applying higher adsorbent dosage. This would result in ineffective adsorption process and low adsorption capacity. The capacity decreases when adsorbent dosage increases due to the increase in surface vicinity and availability of binding sites, which results in some unoccupied sites (Reddy et al., 2016). Further increment of adsorbent dosage does not change much on the adsorption

capacity. This is possibly due to the agglomeration of exchanger particles that causes the overlapping of active sites, which leads to a decrease of effective surface area (Wong et al., 2018).

3.5 Effect of temperature on removal of aspirin from aqueous solution

The result of aspirin removal by ACC at different temperatures (Figure 3c) shows that both percentage removal and adsorption capacity are insignificant factors for aspirin adsorption on ACC. Small changes in aspirin removal were observed, in which the percentage removal and adsorption capacity decreased as the temperature increased. A similar trend was obtained for aspirin adsorption using tire waste adsorbent (Azman et al., 2019). In physisorption process, the interaction between the adsorbate and adsorbent is affected by high temperature. Due to the exothermic nature of adsorption process, the amount of aspirin adsorbed decreases at high temperatures (Wong et al., 2018). In this case, the small changes in percentage removal and adsorption capacity show that aspirin adsorption onto ACC possibly occurs mainly via chemisorption. The interaction and bonding between the adsorbate and adsorbent via chemisorption become stronger at high temperatures (Febrianto et al., 2009).

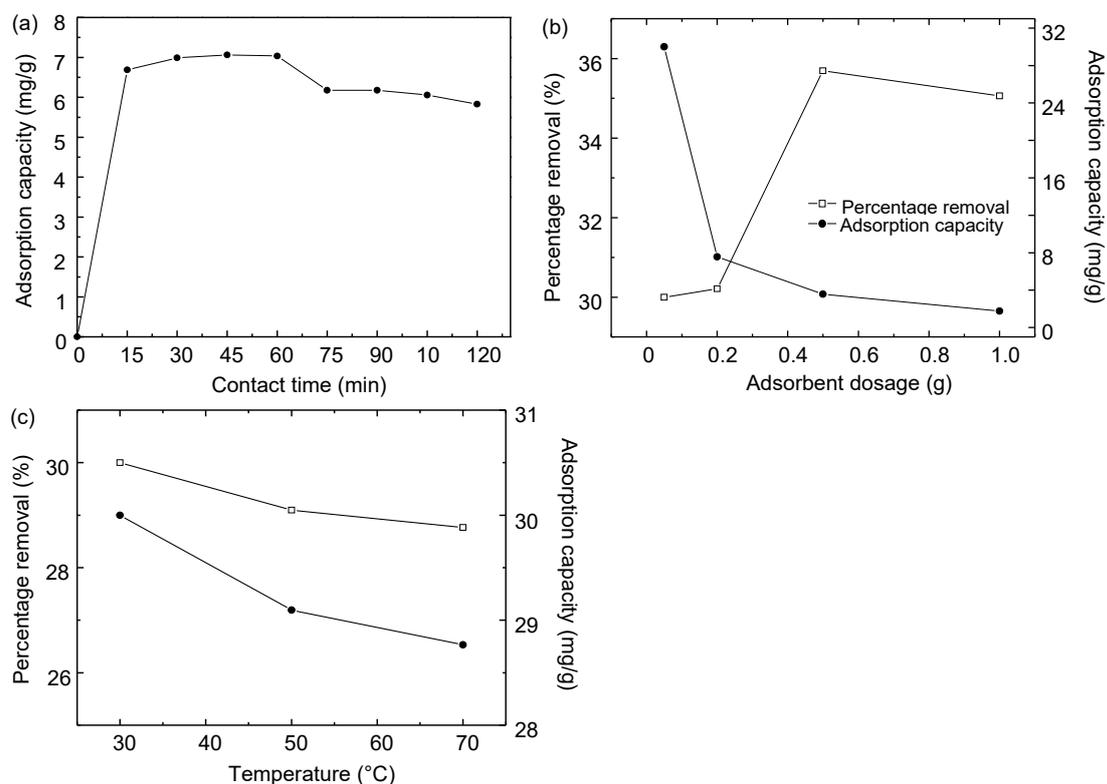


Figure 2: Effects of (a) contact time (pH 6, 60 mg/L, 0.1 g ACC, room temp.), (b) adsorbent dosage (pH 6, 60 mg/L, 45 min, room temp.), and (c) temperature (pH 6, 60 mg/L, 0.05 g ACC, 45 min) on adsorption of aspirin

4. Conclusions

In the present work, ACC was synthesized from urea and furfural and activated by using H_3PO_4 , and the operating parameters for adsorption of aspirin onto ACC were assessed. ACC was successfully synthesized, and its performance as adsorbent in aspirin removal was investigated. In the batch adsorption process, aspirin removal with a maximum adsorption capacity of 30 mg/g was obtained. The best performance was observed at an initial concentration of 60 mg/L, pH 6, and 0.05 g of adsorbent, and the batch process was conducted at room temperature for 45 min. The ACC shows its potential as an adsorbent in pharmaceutical wastewater treatment, and further modification on ACC could be conducted to improve its surface chemistry for high adsorption performance. The adsorption of various pharmaceutical wastes is possible to be conducted using ACC or modified ACC in future work.

Acknowledgments

The authors are thankful to the Ministry of Higher Education (MOHE), Malaysia and Universiti Teknologi Malaysia for funding the project via Research University Grant (RUG) (Q.JI30000.2651.16J62), and for

supporting one of the authors, Muzakkir Mohammad Zainol via Post-Doctoral Fellowship through Professional Development Research University (PDRU) grant scheme (R.J130000.7113.04E78). Special appreciation to Dr. Norzita Ngadi and Mohamed Hizam Mohamed Noor for their help and support on the spectrophotometer analysis.

References

- Azman A., Ngadi N., Zaini D.K.A., Jusoh M., Mohamad Z., Arsad A., 2019, Effect of adsorption parameter on the removal of aspirin using tyre waste adsorbent, *Chemical Engineering Transactions*, 72, 157-162.
- Chegeni M., Mousavi Z., Soleymani M., Dehdashtian S., 2020, Removal of aspirin from aqueous solutions using graphitic carbon nitride nanosheet: Theoretical and experimental studies, *Diamond and Related Materials*, 101, 107621.
- 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.
- Hoppen M.I., Carvalho K.Q., Ferreira R.C., Passig F.H., Pereira I.C., Rizzo-Domingues R.C.P., Lenzi M.K., Bottini R.C.R., 2019, Adsorption and desorption of acetylsalicylic acid onto activated carbon of babassu coconut mesocarp, *Journal of Environmental Chemical Engineering*, 7(1), 102862.
- Hossain A., Nakamichi S., Habibullah-Al-Mamun M., Tani K., Masunaga S., Matsuda H., 2018, Occurrence and ecological risk of pharmaceuticals in river surface water of Bangladesh, *Environmental Research*, 165, 258-266.
- Muhamad M.S., Salim M.R., Lau W.J., Yusop Z., 2016, A review on bisphenol A occurrences, health effects and treatment process via membrane technology for drinking water, *Environmental Science and Pollution Research*, 23, 11549-11567.
- Ouasfi N., Bouzekri S., Zbair M., Ait Ahsaine H., Bakkas S., Bensitel M., Khamliche L., 2019, Carbonaceous material prepared by ultrasonic assisted pyrolysis from algae (*Bifurcaria bifurcata*): Response surface modeling of aspirin removal, *Surfaces and Interfaces*, 14, 61-71.
- Prado T.M.d., Cincotto F.H., Machado S.A.S., 2017, Spectroelectrochemical study of acetylsalicylic acid in neutral medium and its quantification in clinical and environmental samples, *Electrochimica Acta*, 233, 105-112.
- 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.
- Tang C., Shu Y., Zhang R., Li X., Song J., Li B., Zhang Y., Ou D., 2017, Comparison of the removal and adsorption mechanisms of cadmium and lead from aqueous solution by activated carbons prepared from *Typha angustifolia* and *Salix matsudana*, *RSC Advances*, 7(26), 16092-16103.
- Tomul F., Arslan Y., Başıoğlu F.T., Babuçuoğlu Y., Tran H.N., 2019, Efficient removal of anti-inflammatory from solution by Fe-containing activated carbon: Adsorption kinetics, isotherms, and thermodynamics, *Journal of Environmental Management*, 238, 296-306.
- Tran H.N., Wang Y.-F., You S.-J., Chao H.-P., 2017, Insights into the mechanism of cationic dye adsorption on activated charcoal: The importance of π - π interactions, *Process Safety and Environmental Protection*, 107, 168-180.
- 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.
- Yang X., Wan Y., Zheng Y., He F., Yu Z., Huang J., Wang H., Ok Y.S., Jiang Y., Gao B., 2019, Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review, *Chemical Engineering Journal*, 366, 608-621.
- Yang Y.-Y., Zhao J.-L., Liu Y.-S., Liu W.-R., Zhang Q.-Q., Yao L., Hu L.-X., Zhang J.-N., Jiang Y.-X., Ying G.-G., 2018, Pharmaceuticals and personal care products (PPCPs) and artificial sweeteners (ASs) in surface and ground waters and their application as indication of wastewater contamination, *Science of the Total Environment*, 616-617, 816-823.
- Zaini D.K.A., Ngadi N., Azman M.A., Ahmad K., 2019, Utilization of polyethylenimine (PEI) modified carbon black adsorbent derived from tire waste for the removal of aspirin, *Journal of Pharmacy and Pharmacology*, 7, 222-227.
- Zainol M.M., Amin N.A.S., Asmadi M., 2017, Preparation and characterization of impregnated magnetic particles on oil palm frond activated carbon for metal ions removal, *Sains Malaysiana*, 46(5), 773-782.
- Zainol M.M., Nazreen W.A., Ylang P.I.P., Hoe T.T., Yussuf M.A.M., Amin N.A.S., 2020, Ethyl levulinate synthesis from levulinic acid and furfuryl alcohol by using modified carbon cryogel, *Chemical Engineering Transactions*, 78, 547-552.