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Kinetics and Effects of Process Parameters on Oil Adsorption using Activated Carbon from Rubber Seed Kernels (*Hevea brasiliensis*)

Muhammad Aisar Harraz Aswadi[a], Hairul Nazirah Abdul Halim[a,b,*], Nur Farhana Najwa Nasaruddin[a], Siti Khalijah Mahmad Rozi[a,b], Zulfakar Mokhtar[a], Lian See Tan[c], Nurfatehah Wahyuny Che Jusoh[c]

[a]Faculty of Chemical Engineering & Technology, Universiti Malaysia Perlis (UniMAP), Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia
[b]Center of Excellence for Biomass Utilization, Universiti Malaysia Perlis (UniMAP), Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia
[c]Department of Chemical and Environmental Engineering (CHEE), Malaysia - Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia (UTM), Jalan Sultan Yahya Petra (Jalan Semarak), 54100 Kuala Lumpur, Malaysia
hairulnazirah@unimap.edu.my

Wastewater contaminated with oil discharged from food processing industries need to be treated properly in order to avoid clogging the drainage and sewerage systems. The removal of oil via the adsorption technique using biomass as a low-cost adsorbent was proposed in this study. Rubber seed kernels (RSKs) were used as the raw material to synthesise activated carbon. The RSKs were impregnated with 10 wt% of phosphoric acid (H_3PO_4) and carbonised at 500 °C to produce rubber seed kernel activated carbon (RSKAC). Different parameters were included in batch adsorption studies, namely, contact time (30 to 240 min), activated carbon dosage (0.5 to 2.5 g), and temperature (25 to 65 °C). The performance of each process parameter was evaluated based on the adsorption capacity of oil onto the synthesised RSKAC. Pseudo-first order and pseudo-second order models were applied to analyse oil adsorption kinetics using RSKAC. Based on the experimental results, the highest oil adsorption was achieved at 150 min of contact time, 2.5 g of RSKAC, and at a temperature of 35 °C. Oil adsorption using RSKAC in this study followed the pseudo-second order kinetics model. These findings revealed that RSKAC could be synthesised as a low-cost adsorbent for oil adsorption.

1. Introduction

Industrial development and rapid urbanisation have increased wastewater release and contamination level, which resulted from waste disposal problems. As reported by the Department of Environment (DOE), the largest and most significant polluting industries in Peninsular Malaysia with highest produced wastewater are food and beverage companies (40%), rubber factories (14.1%), and chemical manufacturers (11.4%) (Goi, 2020). Wastewater from food production industries generally contains organic matters, with a great quantity of fat, oil, and grease (Klaucans and Sams, 2018). However, without a proper treatment, oily wastewater can have an adverse effect on the surroundings and living things due to pollution in the water sources such as causing pipe clogging and sewage leakage, harming drinking water and groundwater resources, putting human health and aquatic life in danger, and also has an impact on crop production (Abuhasel et al., 2021). Therefore, a proper treatment system for removing oil from wastewater is crucial for the environment.

Various methods and technologies can be used to separate oil from wastewater such as flocculation (Ma et al., 2021), ultrafiltration membrane (Ahmad et al., 2021) and biological treatment (Al Rayaan & Alsyayqi, 2021). However, these processes are costly and can be difficult to operate. Adsorption is the easiest wastewater treatment technique and cheaper (Olufemi and Otolorin, 2017). Most wastewater treatment systems apply activated carbon as the adsorbent; nevertheless, the production cost of commercial activated carbons are quite

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expensive. Activated carbon prepared from natural carbon-rich materials, including agricultural waste and biomass has attracted the attention of researchers, as they have a high potential of effectively eliminating oil contaminants from wastewater. Several biomass materials have been converted into activated carbons, such as corn stigma or corn silk (Mbarki et al., 2022), rubber seed shells (Borhan et al., 2019), and mango shells (Olufemi and Otolorin, 2017).

Rubber seed kernels (RSKs) from rubber trees, *Hevea brasiliensis*, which consist of a high carbon content (64.5 %) (Hassan et al., 2014), is a potential precursor to produce activated carbon due to their availability and abundancy in Malaysia. The literature review conducted in this study showed that a limited number of research has been done on the usage of RSKs as oil adsorbents and the parameters that affect their ability to absorb oil. Thus, the potential of turning RSKs into activated carbon was explored in this research for oil removal applications. In the current research, the effects of contact time, adsorbent dosage, and temperature as well as kinetic studies were investigated to determine the effectiveness and capacity of RSKAC for the removal of palm cooking oil.

2. Methodology

2.1 Materials and chemicals

Rubber seeds were provided by FAE Supply Sdn. Bhd., Malaysia and used as the raw material for synthesising activated carbon. Cooking oil (Knife, Malaysia) was used as the adsorbate in this study, while 85 % ortho-phosphoric acid (H3PO4), and hexane were purchased from Bendosen and HmbG (Germany).

2.2 Preparation of raw material

Dirt on the rubber seeds were removed using distilled water. Then, the seeds were separated into shells, which were discarded, and kernels (RSKs) that were left to dry for 24 h at 100 °C. The RSKs were then soaked in hexane for 15 min to eliminate oils. Once the oils and solvent were discarded, the RSKs were dried again at 100 °C for 2 h. Finally, the RSKs were ground and sieved to 1,000 μm in size, which were then stored in an airtight container.

2.3 Chemical activation and carbonisation

First, 20 g of RSKs were impregnated with 100 mL of 15 wt% of H_3PO_4 for 24 h for chemical activation. Then, the RSKs were placed in an oven to dry for 1 h at 100 °C, and were subsequently carbonised at 500 °C for 1.5 h in a furnace. The resultant rubber seed kernel activated carbon (RSKAC) was cleaned using distilled water until pH 6 to 8 was achieved to remove excess chemicals.

2.4 Batch adsorption test

The effects of process parameters were studied during the adsorption study, namely, contact time, RSKAC dosage, and temperature.

2.4.1 Effect of contact time

The performance of oil adsorption by RSKAC as a result of contact time was studied across time periods ranging from 30 to 240 minutes, with 30-minute intervals. First, 1 g of RSKAC was weighed and poured into a nylon teabag. Second, the teabag was submerged in 20 g of oil, which was in a 100 mL beaker. Third, after the specified interval, the teabag was taken out and was left so the oil from teabag will trickle into a funnel for 15 min. The initial and final weights were recorded to determine the amount of oil that was adsorbed onto the RSKAC. This experiment was performed two more times under identical conditions.

2.4.2 Effect of adsorbent dosage

The effect of adsorbent dosage on oil adsorption using RSKAC was studied in the range of 0.5 to 2.5 g. Teabags with different adsorbent dosages were left in contact with 20 g of oil for 1 h without agitation. Then, each teabag was taken out and was allowed to trickle into a filter funnel for 15 min. Next, the teabag weight was measured and this experiment was repeated two more times.

2.4.3 Effect of temperature

A beaker was filled with 20 g of oil and a teabag containing 1.0 g of adsorbent was placed in the beaker. Then, it was placed in a water bath at different temperature settings (25, 35, 45, 55, and 65 °C) for 2 h without agitation. Then, the teabag was taken out and oil was allowed to drip off, prior to weighing the teabag. This experiment was repeated three times under identical conditions.

2.5 Data analysis

The adsorption capacity (q) of the synthesised activated carbon was analysed based on the amount of oil it has adsorbed per its unit mass, as shown by Eq(1):

$$q = \frac{M_F(g) - M_I(g)}{M_I\ (g)} \tag{1}$$

where M_I refers to the mass of the RSKAC before undergoing adsorption (g) and M_F refers to the mass after undergoing adsorption (g).
The oil adsorption kinetics using RSKAC was analysed using the following pseudo-first order kinetics model in Eq(2) and pseudo-second order kinetics model in Eq.(3):

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \tag{2}$$

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \tag{3}$$

where q_e (mg/g) refers to the amount of oil adsorbed at equilibrium and q_t (mg/g) refers to the amount of oil adsorbed at time *t*. Meanwhile, k_1 and k_2 refer to the rate constant of the pseudo-first order model and the pseudo-second order model.

3. Results and discussion

3.1 Batch adsorption study

3.1.1 Effect of contact time

The effect of contact time from 30 to 240 min on the performance of RSKAC is shown in Figure 1. The lowest adsorption capacity of 0.6253 ± 0.031 g/g was obtained between 30 and 120 min of contact period. During this period, the internal and exterior diffusion of oil particles started to penetrate into the surface of the adsorbent (Ang et al., 2021). The adsorption capacity of RSKAC significantly increased between the period of 120 and 150 min of contact time, reaching a maximum capacity of 0.7479 ± 0.0204 g/g at 150 min. During this timeframe, the oil has successfully diffused into the RSKAC and increased its adsorption capacity. All active sites on the RSKAC surface have been completely occupied by oil after 150 min of being in contact. Then, beyond 150 min, a minor decrease in oil adsorption capacity was observed. This could be attributed to oil desorption from the binding sites, as the number of active sites for oil molecules to attach began to decline (Ang et al., 2021). This finding concurred with the findings reported by Tang et al. (2018).

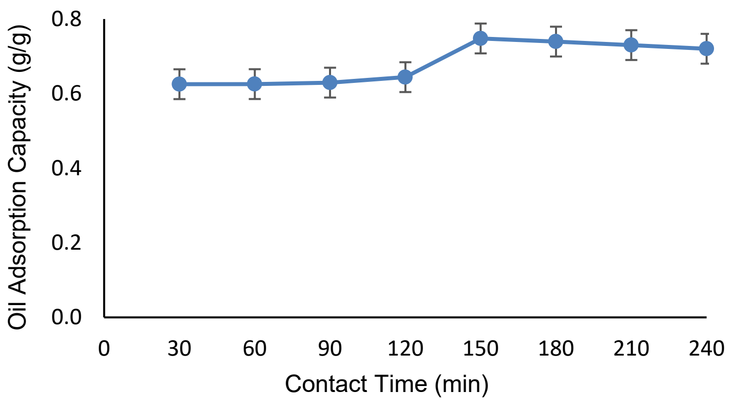

Figure 1: Effect of contact time on adsorption capacity

3.1.2 Effect of RSKAC dosage

The effect of RSKAC dosage on oil adsorption was tested using different RSKAC dosages that ranged from 0.5 to 2.5 g. Adsorption is a surface phenomenon that is directly proportional to surface area, therefore as surface area grows, so does the adsorption (Abdelwahab et al., 2017). As seen in Figure 2, when the adsorbent dosage is increased, the oil adsorption capacity is also increased. The maximum adsorption capacity achieved was 1.136 ± 0.1177 g/g using 2.5 g of adsorbent, whereas the lowest was 0.720 ± 0.0481 g/g using 0.5 g of adsorbent. This noticeable difference was because by increasing the adsorbent dosage, more active sites on the adsorbent surface became available for oil molecules to adsorbed onto (Ang et al., 2021). Thus, a low adsorbent dosage would provide fewer active sites for oil molecules to adsorb, while a high adsorbent dosage can provide plenty of active sites. This observation concurred with the findings of Luvita Sari et al. (2020).

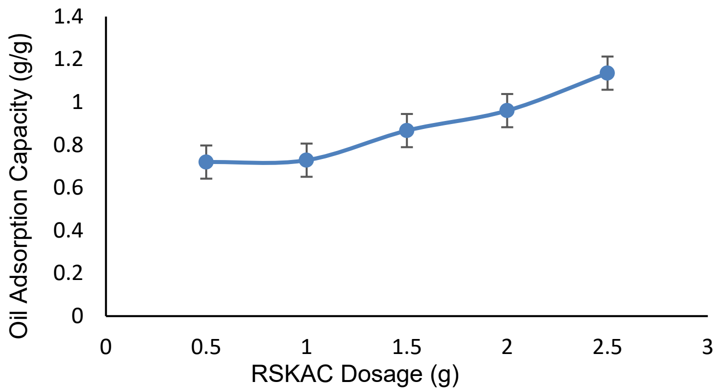

Figure 2: Effect of RSKAC dosage on adsorption capacity

3.1.3 Effect of temperature

Since temperature changes across locations and throughout the year, it is an important aspect to research in wastewater treatment. Figure 3 depicts the effect of temperature on oil adsorption onto RSKAC. The performance of RSKAC increased dramatically between 25 and 35 °C, with the minimum adsorption capacity of 1.0036 ± 0.018 and the highest adsorption capacity of 1.1443 ± 0.059 g/g, respectively. At 35 °C, the kinetic energy of the oil molecules began to increase, and thus, the collision rate between the oil and RSKAC began to increase. In addition, the inner pores of the adsorbent would have expanded due to the increased temperature, which resulted in the high adsorption capacity (Wekoye et al., 2020). However, with increasing temperature from 45 to 65 °C, the adsorption capacity of RSKAC start to decline. This could be attributed to the desorption of oil molecules from the surface of RSKAC. As the temperature continued to increase, the active sites on the adsorbent became more prone to become desorbed and less likely for oil droplets to attach on adsorbent surface because adhering to the surface at higher temperature demands more energy (El-din et al., 2018). The high temperature easily break the weak interaction of Van der Waals between its surface and the oil, hence, affecting the availability of active sites (Anastopoulos et al., 2019).

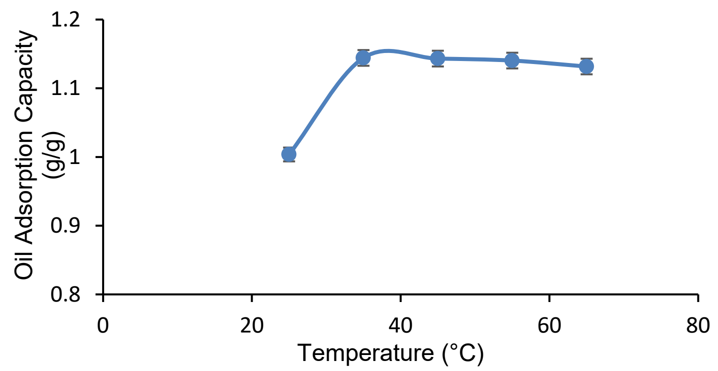

Figure 3: Effect of temperature on adsorption capacity

3.1.4 Kinetic studies

Figure 4 shows the graph for the pseudo-first order kinetics model. In this model, the adsorption rate was assumed to correspond with the number of active sites accessible on the adsorbent surface (Borhan et al., 2019). Table 1 illustrates that the rate constants, k_1 and R^2, of the pseudo-first order model are 0.011515 and 0.227 min^{-1} respectively. Based on the R^2 of 0.6646, this pseudo-first model did not fit the experimental data. The graph for the pseudo-second order model is shown in Figure 5. Table 1 indicates the rate constants, k_2 was 0.098 and the R^2 value of this model was 0.9917, indicating that it fit the experimental data. The pseudo-second order kinetics model describes adsorption as being governed by chemical sorption, or chemisorption (Sahoo and Prelot, 2020). Chemisorption can be increased on adsorbents with larger surface areas, and thus, achieve better oil removal and adsorption.

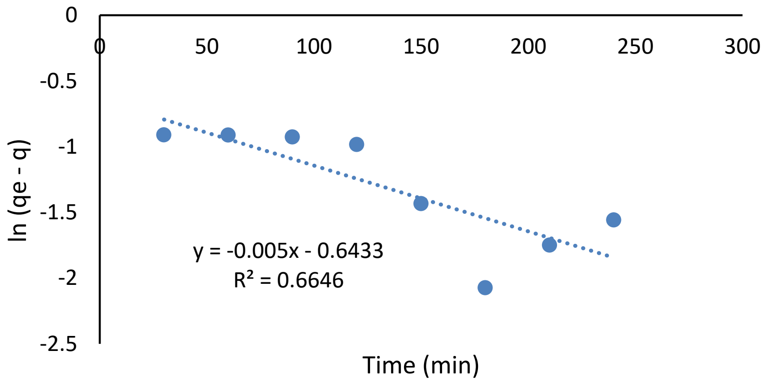

Figure 4: Pseudo-first order kinetics model

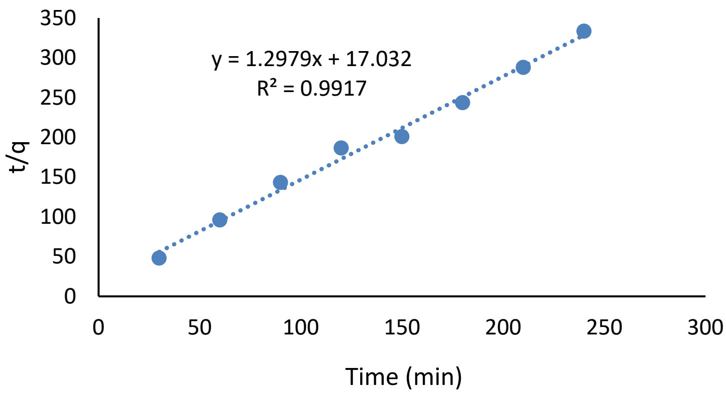

Figure 5: Pseudo-second order kinetics model

Table 1: Rate constant values of kinetics models for oil adsorption

Kinetics model	Parameter	Value
Pseudo-first order	q_e	0.227
	k_1	0.011515
	R^2	0.6646
Pseudo-second order	q_e	0.77
	k_2	0.098
	R^2	0.9917

4. Conclusions

Activated carbon was synthesised from rubber seed kernels in this study. Then, its performance was studied based on the effects of contact time, RSKAC dosage, and temperature in batch operations. The most efficient adsorption conditions were 150 min of contact time, with 2.5 g of RSKAC, and at 35 °C of temperature. The pseudo-second order model was a good fit for oil adsorption using RSKAC. Hence, RSKAC is a potential new adsorbent for oil adsorption.

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