Alkaline activation of marble-like carbon structure and its application for inflammatory adsorption

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Abstract: For the first time, carbon microspheres successfully synthesized by using block copolymer F127 combined with gelatin, sucrose, and H2SO4 as soft template, source carbon, catalyst, respectively. The following step of synthesis are hydrothermal treatment, evaporation, carbonization and pyrolysis treatment under nitrogen flow. Microspheres carbon results have activated by a 10% KOH solution at room temperature for 12, 24, and 48 h, respectively then characterized by SEM and FTIR. The Activated microspheres carbon have used for ibuprofen adsorption. The characterization results showed that carbon microspheres carbon as marbles-like morphology with a diameter of 1-10 μm completed by C-OH, CO2, C≡N, -CNN, C=O, COO−, C=C, CK functional groups as the most. So this study shows that increasing activation time of the microsphere carbon have enhanced the equilibrium time and which is reach equilibrium at range 15-25 min and adsorption capacity range at 55.1-59.9 mg g−1. So carbon microspheres in general conclusion could be potentially as Drug Delivery material.

Keywords: Activation, Gelatin, Microspheres carbons, Time

1.Introduction

Carbons have interesting properties, such as less toxicity, green for organism, high adsorption, obtainability and availability, highsurface areas, orderlyframeworks, narrow pore size distributions, controllability and highthermal stability (J. Wang & Kaskel, 2012). In general, carbon pores can be divided into three groups: macropores, mesopores and micropores. The common form of carbon isdominated by micropores, which arenot completely found in huge molecules, such as ibuprofen. In the case of pollution in ahospital sewage area, removing ibuprofen as a non-steroidal anti-inflammatory drug needs materials with high adsorption capacity and available pores. For this reason, many researchers have synthesised a new type of carbon that has uniformity and large surface area.

In the last few years, the types of carboxpheres, such as nanospheres (CNSS) (Nieto-Márquez, Valverde, & Keane, 2009) and activated carbon microspheres (ACS), have attracted increasingattention due to the advanced material development in the world. Carbon spheres have been applied for drug delivery systems (Zhou, Peng, Liao, Li, & Li, 2014), energy storage (S. Yang et al., 2012), rechargeable lithium-ion batteries (F. Wang et al., 2015), EMI shielding (Meer, Kausar, & Iqbal, 2016) and CNSS (Nieto-Márquez et al., 2009). Methods increasing the pore area have been investigated viaactivation methods. The activation process can be performed using acid solutions, such as HCl (Hanum, O, & Wirani, 2017) and H3PO4 (Guo, Zhang, & Liu, 2016); alkaline solutions, such as potassium hydroxide (KOH)(D. Zhang et al., 2017) and NH4OH (Heidari, Younesi, Rashidi, & Ghoreyshi, 2014); and salts, such as C4H12Si (Pflitsch et al., 2014). Among them, alkaline solutions have
better affinity to carbon surface than others due to the interaction between hydroxide and double-bond carbon. A previous research reported that after an alkaline activation process using KOH, the surface area of a sphere increased from 700 m$^2$g$^{-1}$ to 1622 m$^2$g$^{-1}$ (D. Zhang et al., 2017). KOH has an activator for carbon, such as carbon fibres, carbon nanofibres, CNTs, templated porous carbon, carbide-derived carbon, carbon aerogels and graphene (J. Wang & Kaskel, 2012), not only promotes uniform pore size distribution, pore volume and specific surface area up to 3000 m$^2$g$^{-1}$ (J. Wang & Kaskel, 2012) but also eliminate tar and volatile sites as impurities (Punsuwan, Tangsathitkulchai, & Takarada, 2015). The general optimisation has been investigated in carbon activation by a previous report with focus on varying time, temperature and concentration (H. M. Yang, Zhang, Chen, Ran, & Gu, 2017) and oxidation time (Kyzas, Lazaridis, & Deliyanni, 2013). However, the long activation period of carbon spheres has been rarely investigated before.

In previous reports, carbon spheres were synthesised through inverse microemulsion solvothermal (Mi & Liu, 2009), hard templating (Li et al., 2011) and soft templating (Görka, Fenning, & Jaroniec, 2009). Soft templating is a gel-sol method, which involves a surfactant for directing the structure (Maria Ulfa, 2017), is a favourable method due to its low cost, simplicity and high controllability (Xie, Kocae, Chen, & Kocae, 2016). The poor characteristics of synthetic templates, such as the triblock poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymer Pluronic F127 (Görka et al., 2009; J. Yang et al., 2010), triblock copolymer poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) Pluronic PI23 (Han, Zhou, Lin, & Zhu, 2013; Arab, Badiei, Koolivand, & Mohammadi Ziarani, 2011), cetyltrimethylammonium bromide and cetyltrimethylammonium chloride (Görka et al., 2009; Paik, Mastai, Kityk, Rakus, & Gedanken, 2012) are not easily degraded by microorganisms and water, which has a bad impact on the environment. Synthetic templates can be replaced by natural soft template materials (Hosseinzadeh, Khorsandi, & Hemmaty, 2013). Natural soft templates have been used in several studies, such as those on starch, gum arabic (Maria Ulfa, 2017) and gelatine (Pongsendana, M et al., 2017). Gelatine was successfully used as a carbon precursor to synthesise a high-surface-area mesoporous carbon (Pongsendana, M et al., 2017) and carbon foams (M. Ulfa & Ulfa, 2018). Gelatine can produce high-performance materials, are low cost and nontoxic and have high levels of carbon content (B. Xu et al., 2012). To the best of our knowledge, no investigation has used gelatine as a sphere template before.

Here, synthesised carbon microspheres (MCS) were used as soft natural composite templates of the block copolymer Pluronic F127 and gelatine. We used sucrose and H$_2$SO$_4$ as sources of carbon and catalysts. Afterwards, the obtained carbon microspheres were activated by KOH to open the pores and increase the surface area. A varying time was applied on the sample to investigate the effect on the morphology and performance. Finally, the kinetic performance of ibuprofen was investigated and the adsorption capacity of the carbon sample was measured.

2. Methods

2.1 Materials

This study used the following materials for analysis: absolute ethanol (Merck’s EMPARTA: CAS number 64-17-5; EC index number 603-002-00-5; EC number 200-578-6; Grade ACS, ISO and Reag. Ph Eur from Sigma Aldrich) with a molecular weight of 46.07 g/mol, boiling point of 78.3 °C, melting point of −114.5 °C, density of 0.790–0.793 g/cm$^3$ (20 °C) and flash point of 12 °C; distilled water; sucrose ≥ 99.0% (HiMedia Laboratories Pvt.Ltd.: CAS number 57-50-1; EC number 200-334-9), with a molecular weight of 342.30 g/mol; triblock poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymer Pluronic F127 from Sigma with a melting point of 53 °C–57 °C and flash point >150 °C; H$_2$SO$_4$ 95%–97% (Merck’s EMUSE: CAS number 7664-93-9; EC index number 016-020-00-8; EC number 231-639-5-6; Grade ACS, ISO and Reag. Ph Eur from Sigma Aldrich) with a molecular weight of 98.08 g/mol, density of 1.84 g/cm$^3$ (20 °C) and melting point of −22 °C; n-hexane (Merck’s EMUSE: CAS number 110-54-3; EC index number 602-037-00-4; EC number 230-777-6-6; Grade ACS, ISO and Reag. Ph Eur from Sigma Aldrich) with a molecular weight of 98.08 g/mol, density of 1.84 g/cm$^3$ (20 °C) and melting point of −20 °C; technical gelatine (Sigma Aldrich: CAS number 9000-70-8) with pH 6.0, density of 0.68 g/cm$^3$ (water = 1) and molecular weight of 60000 g/mol; and ibuprofen ≥98% (Sigma Aldrich: CAS number 15687-27-1; EC number 239-784-6) with a molecular weight of 206.28 g/mol.
2.2 Material Synthesis
Carbon microspheres were synthesised by the following procedure. First, 15% of Pluronic F127 was mixed with 92% ethanol and 39% water (% w/w). After the ethanol was poured, the mixture was stirred for 2 hours under closed condition. Then, 4% sucrose and 7% gelatin were added to a solution of triblock poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymer Pluronic F127, which has been formed and stirred for 2 hours. Then, a few drops of sucrose solution (9% sucrose, 45% water and 4% H₂SO₄) was stirred for 24 hours. Then, the synthesis results were placed into a hydrothermal autoclave reactor and in the oven under 100 °C temperature for 30 hours. The resulting brown solution was placed in a porcelain oven at temperature of 100 °C 6 hours and then at 160 °C for 18 hours to form dried black solids. The black solids were crushed and sieved using an 80-mesh screen to form black powder. Finally, pyrolysis was performed on the black powder accompanied by nitrogen flow for 5 hours at a temperature of 800 °C. As a result, carbon black powder microspheres (MCS) were obtained. The activation process was conducted by mixing MCS with KOH and stirring for 30 minutes at room temperature (29 °C) in a closed condition. The mixture was formed allowed to stand for periods of 12, 24 and 48 hours. After soaking, the mixture was filtered through Whatman paper. The filtered water from the solids was evaporated in an oven at 100 °C temperature for 24 hours, and then, the washing process was performed. Carbon solids produced inactive microspheres, called AMCS-\(x\) h, where \(x\) is the activation time.

2.3. Ibuprofen Adsorption
The ibuprofen adsorption process was performed by mixing ibuprofen carbon microspheres and a solution with a stirrer at room temperature (29 °C) and in a closed condition with an interval of 5 minutes. The results of the UV–vis spectrophotometry were plotted into a calibration curve of absorbance against the concentration to obtain a linear relationship according to Beer–Lambert law. To determine the amount of ibuprofen that can be absorbed, the following equation was used:

\[
q_t = \frac{C_0 - C_t}{W} \times V,
\]

where \(q_t\) is the amount of ibuprofen adsorbed during a certain time (mg g\(^{-1}\)), \(C_0\) is the early concentration of ibuprofen (ppm), \(C_t\) is the concentration of ibuprofen in a certain time (ppm), \(V\) is the volume (litre) of a solution of ibuprofen and \(W\) is the weight (g) of activated carbon. The linear regression analysis is determined by the following formula:

\[
\frac{C_0}{q} = \frac{1}{q_{\text{max}}.W} + \frac{C_0}{q_{\text{max}}}
\]

D. Characterisation
Characterisation was performed to determine the morphology of ACS by using images taken with a JEOL JSM-700 scanning electron microscope (SEM) at a speed of 15.0 kV. The functional groups contained in the ACS were characterised using Fourier transform infrared (FTIR) spectra and recorded with a Bruker Vertex 70 spectroscope at a wavelength of 500–4000 cm\(^{-1}\). Then, the absorbance of the samples taken in 5-minute intervals was determined via UV–vis spectroscopy (model U-2000, Hitachi, Japan) at a wavelength of 272 nm.

3. Results And Discussion
Carbon was used as the adsorbent in the ibuprofen adsorption and activation process using the KOH solution for 12, 24 and 48 hours. The weight of the initial carbon significantly increased due to the potassium aggregation from the activator and water in the surface. The contradiction was showed by the decreasing carbon mass after increasing the activation time.
Figure 1. Deposition process of potassium, water and impurities in the carbon and release of potassium from the carbon: a) AMCS-12 h, b) AMCS-24 h and c) AMCS-48 h.

Figure 1 shows the potassium deposition process onto carbon at different periods of time. As shown in Fig. 1a, the diffusion of molecules of potassium, water and other particles (impurities) in the outer carbon surface was gradually finished by the aggregate deposition. Moreover, after activation of 24 h, the exposed aggregate was gradually released and then some slit and space of the carbon was generated by the removal of potassium ions, water molecules and other particles during the washing process. Hence, the long activation period can be the stimulator for the microspace formation. A similar phenomenon is also observed in AMCS-48 h, where numerous potassium ions leached out from the inner and outer surfaces. This process has big impact on the carbon weight degradation. In addition, the weight change of the AMCS samples was clearly influenced by the long activation process period.

Figure 2. Results of FTIR characterisation of carbon microspheres: a) AMCS-12 h, b) AMCS-24 h and c) AMCS-48 h.

The C-OH group at 3394 cm⁻¹ (H. Zhang, Xu, Yang, & Geng, 2010), antisymmetric CO₂ at 2350 cm⁻¹ (H. Zhang, Xu, Yang, & Geng, 2010), C≡N at 2173 cm⁻¹ (H. Zhang, Xu, Yang, & Geng, 2010), C=O stretching of carboxylic acids at 1640–1725 cm⁻¹ (Krumins, Klavins, Seglins, & Kaup, 2012), asymmetric COO⁻ at 1594 cm⁻¹ (Nunes, Reva, Fausto, Bégué, & Wentrup, 2015), aromatic C=C at 1488 cm⁻¹ (Tinti, Tugnoli, Bonora, & Francioso, 2015) and CK group at 515 cm⁻¹ (Periasamy, Muruganand, & Palaniswamy, 2009). The adsorption bands of the AMCS samples at 3394, 2344, 2130, 2087, 1710, 1593 and 4000–300 cm⁻¹ can be ascribed to the stretching vibration of the C-OH, CO₂, C≡N, −CNN, C=O, COO⁻, C=C, CK and hydroxyl groups (O–H) involved in the hydrogen bonding and/or water adsorption on the carbons (H. Zhang, Xu, Yang, & Geng, 2010; Hao, Bechtel, Kneafsey, Gilbert, & Nico, 2018; Blouin, George. C., & Olson, John. S., 2010; Nunes, Reva, Fausto, Bégué, & Wentrup, 2015; Krumins, Klavins, Seglins, & Kaup, 2012; N. Peys et al., 2014; Tinti, Tugnoli, Bonora, & Francioso, 2015; Periasamy, Muruganand, & Palaniswamy, 2009). The peak at 1550 cm⁻¹ may be assigned to the asymmetric COO⁻ vibrations of carbon, whereas that at 1457 cm⁻¹ may be attributed to the C=C bond of aromatic rings, which is only shown for the spent carbons.

As shown in Fig. 2, all samples have a similar fundamental peak, which means that no significant characteristic is observed in the functional group of all samples at different activation times. The functional groups in AMCS-12 hours are C-OH, CO₂, C≡N, −CNN, C=O, COO⁻, C=C and CK, which are connected to 3657.11, 2370.35, 2161.44, 1970.69, 1700.48, 1605.10, 1457.50 and 509.84 cm⁻¹, respectively. Meanwhile, the functional groups of AMCS-24 hours are C-OH, CO₂, C≡N, −CNN, C=O, COO⁻, C=C and CK, which correspond to 3631.38, 2352.94, 2161.44, 1970.69, 1700.48, 1552.88, 1465.83 and 518.17 cm⁻¹, respectively. The functional groups at on AMCS-48 hours are C-OH, CO₂, C≡N, −CNN, C=O, COO⁻, C=C and CK, which correspond to 3631.38, 2370.35, 2178.85, 1970.69, 1700.48, 1561.96, 1475.50 and 500.76 cm⁻¹, respectively.

The AMCS-12 h results show that the carbon content of the OH group is more than that in AMCS-24 h and 48 h. Thus, the decrease in the carbon content of OH greatly affected the carbon weight at the end of the activation process. In addition, the functional groups, such as C-OH, −CO₂, C≡N, −CNN, C=O, COO⁻, C=C and
CK, were contained in the AMCS-12 h more than AMCS-24 h and 48 h. This finding is attributed to the washing process, where most of the potassium ions in AMCS-12h still adhere to the surfaces and crevices of carbon escape in the potassium leaching process. As for AMCS-24 h and 48 h, potassium ions were affixed to the surface and the carbon gap shrunk, and the time of the potassium leaching process will dissolve along the water, causing the group content AMCS-24 h and 48h slightly.

Figure 3. SEM characterisation results of AMCS-12 h

Figure 3 shows the SEM image of the AMCS sample. The AMCS-12 h sample carbons underwent greater destruction compared with the AMCS-24 h and 48 h surfaces (not shown). The carbon particles at the surface were destructed by the potassium ions and OH group. Small carbon particles were generated by numerous potassium ion released during the washing process. The resulting carbon samples after the activation process have a high adsorption performance due to the slit formation from the leaching process. Thus, the long activation time not only opened the outer surface of the carbon microspheres but also acted as the template for the new pore formation.

Table 2 shows the marble-like particles that were observed by the SEM. According to the results of the SEM characterisation, the increasing time of the activation of the carbon microspheres with KOH resulted in the carbon surface being covered with potassium ions. Moreover, the activation time declined, causing damage to the particles on the surface of the carbon: AMCS-12 h at 19%, AMCS-24 h at 13% and AMCS-48 h at 12%. The amount of damaged particles measuring 2–5 μm on the surface of AMCS-12 h was the highest compared with the broken particles on the surface of AMCS-24 h and 48 h. This finding indicates that tiny particles measuring 2–5 μm have high potential to adsorb ibuprofen. Thus, the adsorption performance in AMCS-12 h is very good. Pictures of the adsorption performance of AMCS-12 h, AMCS-24 h and AMCS-48 h are shown in Figure 4.

Figure 4. Adsorption performance of a) AMCS-12 h, b) AMCS-24 h, c) AMCS-48 h.

Figure 4 shows the adsorption performance of the activated carbon microspheres. The increasing adsorption time affected the decreasing ibuprofen concentration at an equilibrium condition. The equilibrium concentration at 12, 24 and 48 h gradually decreased in the first 15 min with ibuprofen concentration of 22.68, 18.73 and 18.67 mg kg⁻¹, respectively. Thus, the increasing equilibrium state at a certain time was affected by the activation time enhancement. At the time of the activation process of carbon for 12 hours, potassium ions were deposited and attached to the carbon surface, causing much ibuprofen and potassium ions to bound to the surface and split into small carbon particles. The ibuprofen adsorption process in AMCS-12 h, AMCS-24 h and AMCS-48 h was obtained at equilibrium and maximum capacity (qmax) when the carbon microspheres adsorbed ibuprofen.
Figure 5 shows the relationship between the time of equilibrium and $q_{\text{max}}$ of the activated carbon microspheres. The increasing activated carbon microspheres were affected by the activation time enhancement. This phenomena can be illustrated by the flat surface of the carbon surface, which is composed of potassium ions, water molecules and other particles (impurities) covering it. The phenomena can be proven by the decreasing weight of AMCS after 24 h. Table 3 that in every activation process after 12 h, the weight of the AMCS samples decreased to closely 10%. The activation process was completed for 12 hours, and the carbon surface was covered with numerous potassium ions, water molecules and other particles (impurities) with a carbon weight after activation of 0.87 grams. Thus, the ibuprofen molecules easily interacted to the carbon surface by the potassium ions. Potassium can act as an active site to build a physical bond and electrostatic interaction bond with ibuprofen. Thus, with the presence of ibuprofen, which is bound to the surface and carbon gap, the time needed to reach equilibrium is getting faster, which is 15 minutes. By contrast, at the carbon activation for 24 hours, the surface and carbon gap were plastered but not as much potassium as when the carbon activation process for 12 hours with carbon weight after 24 hours of activation of 0.76 grams. Potassium, which is bound to carbon, is not too much, causing a large amount of ibuprofen to be adsorbed, mostly on the surface and carbon gap. Thus, in the less helpful potassium adsorption process, the time needed to reach equilibrium increasingly slowed to 20 minutes. When the carbon activation process was carried out for 48 hours, the carbon surface was covered by numerous little potassium ions with carbon with an activation weight of 0.60 grams. When very little potassium ions bound to carbon, a small amount of ibuprofen is adsorbed, and almost all ibuprofen particles are adsorbed on the surface and carbon gap. As a result of the presence of potassium, which is not optimal when helping the adsorption process, the time needed to reach a balanced state slows down to 25 minutes. The maximum adsorption capacity of ibuprofen has increased during AMCS-12 h towards AMCS-24 h, with an increase of 2.86 mg g$^{-1}$. The maximum capacity of AMCS-24 h is greater than AMCS-12 h because the AMCS-24 h surface is not much damaged. Thus, ibuprofen can be directly adsorbed on the carbon surface more than on the surface of AMCS-12 h, which has the most damage. The maximum adsorption capacity of AMCS-48 h is almost the same as that of AMCS-24 h, which is equal to 57.99 mg g$^{-1}$ and 57.98 mg g$^{-1}$, respectively, with a difference of 1%. This result is attributed to the damages to the AMCS-24 h and AMCS-48 h surfaces, which are more evident than that at the AMCS-12 h surface. As a result, ibuprofen was adsorbed more directly by the carbon surface than in the AMCS-12 h surface. The maximum adsorption capacity of ibuprofen was observed in the AMCS-24 h surface because not much damage is done to the carbon surface and particles in the size of 2–5 µm. Both of these cases caused much damage to the maximum adsorption of ibuprofen to the carbon surface and particles in the size of 2–5 µm.
Figures 5 and 6 show that the carbon activation time and maximum adsorption capacity will be increased and will reach a maximum and equilibrium upon activation for 24 hours. The equilibrium curve at the maximum adsorption capacity was attributed to the damage caused by the particles on the carbon surface in AMCS-24 h and 48 h, which have only 1% difference in the extent of damage to the particles. As a result, the adsorption capacity reached 57.99 and 57.98 mg g\(^{-1}\). Likewise, the weight of carbon after activation decreased when the activation time increased. This finding corresponds to the research of H. M. Yang, Zhang, Chen, Ran and Gu (2017), who found that if the activation time is over 2 hours, then the amount of activated carbon weight decreases.

The data in Figure 7 show that the Langmuir equation (\(C_e/q_e\) versus \(C_e\) opponent) for the adsorption of ibuprofen on AMCS-12 h, AMCS-24 h and AMCS-48 h produce great results with the linear regression analysis equations. Langmuir’s adsorption isotherm equation shows good views of the linear regression coefficient (\(R^2\)) of 0.9977 for AMCS-12 h, AMCS-24 h and AMCS-48 h. The maximum capacity occurs in AMCS-24 h at 57.99 mg g\(^{-1}\). The maximum capacity in AMCS-24 h can be due to the damage to the AMCS-24 h, which is 13%. This finding supports the adsorption of ibuprofen. Thus, the maximum adsorption capacity was influenced by the average activation process.

4. CONCLUSION

In this study, the synthesis of carbon microspheres (MSC) was successfully performed using soft templates, such as triblock poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymer Pluronic F127 combined with gelatine, sucrose and \(\text{H}_2\text{SO}_4\). MCS was successfully synthesised using KOH activated by variations in time to produce AMCS-12 h, AMCS-24 h and AMCS-48 h. After characterisation by using FTIR, the AMCS group included C-OH, C=O, CO\(_2\), C≡N, −CNN, C=O, COO\(^-\), C=C and CK. Meanwhile, the SEM results show that the marble-like particles in the AMCS had a size of 1–10 μm, with an average particle size at <1 μm. The large particles broken in AMCS-12 h were 19%, AMCS-24 h were 13% and AMCS-48 h were 12%. The AMCS particle damage was due to the influence of carbon activation with KOH, and the surface of the AMCS also adsorbed potassium ions, water and impurities. Based on the results of the activation process, when the adsorption process was carried out, the ibuprofen adsorption had a maximum capacity of 57.99 mg g\(^{-1}\) in AMCS-24 h and 57.98 mg g\(^{-1}\) in AMCS-48 h. Thus, if the time of MSC activation is longer, then the adsorption capacity is in the range of 57.90 mg g\(^{-1}\) for AMCS-24 h until equilibrium. Thus, its adsorption capacity is large.

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