Activation of carbon at different concentration microsphere adsorbent and its application for ibuprofen adsorption

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Abstract: A synthesis is presented in this research, microspheres carbon by mixing Pluronic F127 triblock copolymer, which was used as a main pore size direction, gelatine as a codirecting agent, Sucrose becomes the main ingredient of carbon precursor and H2SO4 be a catalyst. The mixture solution carried out at hydrothermal reactor followed by evaporation, partial carbonization, and pyrolysis under nitrogen flow. After being microspheres carbon have activated by KOH solution at room temperature for 24 h using a variation of the KOH concentration at 5, 10, 15 and 20 (%w/v), respectively. Activated Microspheres carbon have characterized by SEM and FTIR. In this study, it was found that carbon mass after activation is increased due to the deposition of potassium and a free water molecule. The morphology of microspheres carbon after activation process observed as soccer balls-like with pore size 0.5-15 µm with numerous of carbonyl and hydroxyl group. In this study, it was found that the greater the activator concentration, the greater the adsorption capacity, due to potassium deposition and water molecules. Maximum adsorb capacity is at 20% KOH concentration at 35 minutes. Microspheres for drug delivery systems are interesting to study.

1. Introduction
Carbon microspheres have attracted many interests for study due to the unique character such as specific height regarding surface area, high specific catalytic, ordered structure and uniform shape of spheres [1]. The Carbon microspheres not only used as a catalyst may also act as a carrier material in a drug delivery system for the last ten years [2]. Carbon microspheres have been used for anchor sites for numerous types of drugs, small molecules, proteins, vaccines, and nucleic acids[3]. In the delivery system, carbon microspheres have been observed as a drug delivery carrier which has high bioavailability, high release performance and high biocompatible due to the easy pore control [4]. However, the synthesis of carbon microspheres complicated and requires a high cost.

One of the methods for synthesis carbon microspheres is soft-templating which is have not required a porous membrane for nanostructures formation [5]. The soft-template method is a simple technique due to the self-arrangement structure by an interaction between organic molecules and precursor via hydrogen bonds, π-π interactions, Van der Waals forces and electrostatic forces[5]. Soft-template method not only stimulates the growth of nanoparticles room to grow [6]but also assemble-able from one-dimensional nanostructures into three-dimensional[5]. n common, Soft-template was used several organic synthetic molecules as Pluronic F127 (F127) [7]. n common, Soft-template was used several organic synthetic molecules as template such pluronic F127) [8]. Tergitol L-62[9]. Synperonic F
However, these materials are expensive, not renewable and unbiodegradable in an aquatic environment.

The problem could be solved by replacing the synthetic organic molecule with a soft-natural template, gelatin is one of organic molecule that has a similar character with a synthetic organic molecule such as hydrophobic-hydrophilic sites, long chain, high weight molecule and high affinity to the precursor. Gelatin generated by partial hydrolysis of collagen, extracted bone sawt and tissues in animals as animal protein extraction which is available in nature, low cost, biodegradable, high solubility in water and can be a catalyst for the transformation of the base sites have free NH2[11-13].

Ibuprofen is a non-steroidal anti-inflammatory drug which is commonly used as pain decreaser[14]. During ibuprofen delivering on body system a lot of problems and bad effects such as on gastrointestinal and kidney function was obtained by periodical ibuprofen consumed. In addition, ibuprofen is used in a long period of time can inhibit prostaglandin and prostacyclin that can increase blood pressure due to renal vasoconstriction [15]. However, waste ibuprofen may be contaminants in the water and difficulty in handling.

In this study, we use chemical activation, because the process is shorter than the physical activation and can be done at high temperatures and time is also short[16]. Allows the chemical activation, the surface area of the carbon we obtain higher and the results are much better [16]. The most effective activated carbon in production with KOH [17]. When the activator concentration increases resulting in increased ion species and ion mobility restrictions resulting in delay clot formation structure [18]. When the concentration of activators increase the formation of the polymer becomes too late [18]. To our knowledge, an investigation has not been conducted regarding the relationship of structural material and activator concentration.

This work studied Carbon microspheres synthesis soft-template technique using triblock copolymer Pluronic F127 the main pore size director, gelatin as a natural template as well as co-template, sucrose as a carbon contributor becomes a precursor and sulfuric acid as a catalyst. The step of carbon microspheres synthesis involving evaporation, hydrothermal, the partial carbonization and pyrolysis process under nitrogen flow. Carbon microspheres activation using KOH solution with various variations of concentrations at 5, 10, 15 and 20 (% w / v), respectively, at room temperature for 24 hours. SEM and FTIR are used to characterize Activated Carbon Microspheres (AMC).

2. Methods
2.1 Material
The material used is as follows: Ethyl Alcohol (CH3CH2OH), relative density of 0789 g / mL at 25 ° C purchase at SIGMA-ALDRICH; pluronic F-127, pH 6.0 - 7, purchase at SIGMA-ALDRICH; Gelatin, pH 4.0 to 7 at 66.7 g / l at 60 ° C, purchase at SIGMA-ALDRICH; Potassium hydroxide (KOH), Relative density 2.044 × 10^-6 g / m^3, pH 13.5, purchase at SIGMA-ALDRICH; H2SO4, Relative density 1.84 × 10^-6 g / m^3 at 298 K, purchase at SIGMA-ALDRICH; Sucrose pH 5.5 to 7.5 at 342 g / l at 298 K, purchase at SIGMA-ALDRICH.

2.2 Material Synthesis
Carbon microspheres are synthesized with ethanol and water dripping into the F127 with a ratio of ethanol: water: F127 amounted to 0.60: 0.26: 0.10 (% w / w), after mixed and then stirred 2 hours. After that adding sucrose: gelatin at 3: 0.10 (% w / w) then stirrer 2 hours. Then do dripping with sucrose solution: water: H2SO4 of 0.20: 0.05: 0.1 (% w / w) while stirrer 24 hours. And then inserted into a hydrothermal reactor while the oven 1000C for 24 hours. After the continuous drying in a 1600C oven for 6 hours to yield a dark solid. The solid was crushed and then in the sifter into carbon microspheres (MC) in the form of fine powder. MC then calcined at 8000C nitrogen stream for 5 hours.

2.3. Ibuprofen Adropsi
Adding AMC-y with y: 5, 10, 15, 20 (% w / v) hexane into a solution of Ibuprofen with 100ppm. Stirred at room temperature while the solution was taken 3ml every interval of 5 minutes to search for using UV-Visible absorbance. Then create a calibration curve of absorbance vs. concentration to obtain a linear equation. The equation obtained is linked to the Lambert-Beer equation as follows:

\[ q_t = \frac{C_0 - C_t}{w} x v \]

Information:
- \( q_t \) = amount of ibuprofen that is absorbed at a certain time (mg g\(^{-1}\))
- \( C_0 \) = initial concentration of ibuprofen (ppm)
- \( C_t \) = The concentration of ibuprofen when a certain time (ppm)
- \( w \) = Mass of carbon microspheres before activation (g)
- \( v \) = ibuprofen in hexane solvent (ppm)

To get the maximum capacity data AMC in adsorbing ibuprofen using the following formula:

\[ q_e \text{ max} = \frac{C_0 - C_{\text{max}}}{w} x v \]

- \( q_e \text{ max} \) = maximum amount of ibuprofen by MC (mg g\(^{-1}\))
- \( C_0 \) = ibuprofen initial concentration (ppm)
- \( C_{\text{max}} \) = Maximum Concentrations of ibuprofen when a certain time (ppm)
- \( w \) = Mass of carbon microspheres before activation (g)
- \( v \) = ibuprofen in hexane solvent (ppm)

But it also can use the following formula[19]:

\[ \frac{C_e}{q_e} = + \frac{1}{q_{\text{max}} K_1 q_{\text{max}}} \]

2.4. Characterization

Characterization using: Scanning Electron Microscope (SEM) JEOL JSM-700 kV HV 15.00 to determine the morphology of AMC-y; FTIR or its abbreviation is Fourier Transform Infrared Spectroscopy, this spectra recorded at a wavelength of 500-4000 cm\(^{-1}\) to determine the functional groups within the AMC-y; and UV-Visible Model U-2000 Hitachi Japan to determine the absorbance which is used to calculate the capacity adsorp.

3. Results and Discussion

Table 1. The mass of carbon microspheres before and after activation

| W (weight) | AMC-5% | AMC-10% | AMC-15% | AMC-20% |
|-----------|--------|---------|---------|---------|
| Before Activation | 0.07 g | 0.07 g  | 0.07 g  | 0.07 g  |
| After Activation  | 0.387 g| 0.617 g | 0.738 g | 1.098 g |

Table 1 shows the mass sample after activation. The initial mass for all sample is 0.07 g. After the activated carbon microspheres with KOH (AMC) are different variations of carbon microspheres mass increased by about 10%. Mass carbon microspheres increase as well as increasing KOH concentrations. Carbon Mass has been changed before and after activation due to the deposition of potassium, water, and also impurities into carbon microspheres. The cause of mass deposition of carbon microspheres is increased. The greater the activator concentration time of activation, the greater the mass, it is because the greater the concentration of the greater number of potassium so did the water of impurities that can be absorbed by the carbon microspheres.
**Figure 1.** The process of deposition of potassium, water and impurities in the carbon microspheres with various concentrations of KOH activation.

Fig 1 shows the content of the sample which is potassium, water, and also there are impurities deposited into carbon microspheres. Fig 1.a clearly shows that AMC-5% have the lowest amount of potassium and water which are deposited into carbon microspheres due to lowest activator concentration. The impurities in AMC-5% generated not only from precursor but also calcination reactor which is less element involved by high-temperature treatment. Fig 1.b-d shows the interesting phenomenon which is increasing activator concentration followed by increasing impurities deposition due to the accessible pore for the high amount of activator element. In our prediction, during the activation process, potassium from activator. There is the mass change in Table 1 clearly explained by an illustration in Fig 1 which is increasing impurities amount not only deposited by activator but also water and other particle form side reaction. It is logic when AMC synthesis using colloidal synthesis system which is have a high affinity for hydrophilic interaction between a water molecule and impurities from a precursor. The framework change was observed by scanning electron microscopy in Fig.2

![Micrograph of AMC-5%](image1)

- **a) AMC-5%**
  - MC, 2.5 μm
  - Aggregate, 12.5 μm consists of 20 soccer balls-like

![Micrograph of AMC-10%](image2)

- **b) AMC-10%**
  - Aggregate, 15 μm consists of 11 soccer balls-like and clots of KOH, water, and impurity
  - MC, 5 μm
Figure 2. Characterization Scanning Electron Microscope (SEM) concentration variation respectively.

Fig 2 shows the SEM image from AMC at varying activator concentration. Fig 2.a explain AMC-5% sample small size aggregate up to 12.5 µm as well as twenty football clustered-like structure. The morphology of carbon microspheres AMC-5% as looks as a football-like aggregate with numerous. As can be seen at Fig 1.a-d, all samples show the destruction part up to 25%. it was similar to our prediction before which was the droplet formation between gelatin, a block copolymer, and carbon precursor which would be damaged by the repulsive attraction from the hydrophobic sites from each element. The destruction process is significantly activated by high interaction between activator and carbon sample processes. It is strongly proofed by increasing destruction as well as increasing activator concentration. Fig 2.b shows AMC-10% having aggregates size closely to the 15µm with eleven footballs-like structure. The aggregate clusters like in our prediction generated by deposition of potassium, H2O molecule and small impurities which are some empty areas greater than AMC-5%. The damage caused by Potassium in image form clumps of white-AMC is more than 5%. The interesting phenomenon observed in Fig. C-d that shows a similar trend with the lowest activator sample. The structure of AMC-15% and AMC-20% have particle size close to 7.5µm, 12.5µm which is imply that increasing activator concentration and impurities will be followed by increasing aggregate carbon structure. In our prediction, aggregation has been stimulated by increasing activator concentration due to limiting mobility in potassium in carbon surfaces. We can conclude that the highest activator concentration has a big impact on the lowest distance of carbon particle and impurities aggregation. The rich of potassium ion was successfully infiltrated onto the carbon framework and micro space generated by the reaction.
side of activation after the washing process. The detailed analysis shows by table 2 for observation comparison sample.

| Surface Size Amc (µm) | AMC-5% | AMC-10% | AMC-15% | AMC-20% |
|-----------------------|--------|---------|---------|---------|
| <2.5                  | 10     | 21      | 25      | 33      |
| <5                    | 26     | 33      | 36      | 42      |
| <7.5                  | 30     | 45      | 43      | 48      |
| <10                   | 6      | 10      | 11      | 13      |
| <12.5                 | 4      | 6       | 7       | 9       |
| <15                   | 2      | 3       | 4       | 5       |

Table 2 shows the analysis morphology image from all sample. As we can see, AMC 20% have had the highest destruction part due to the high potassium particle in carbon. Potassium in our prediction was deposited during the activation process then interact with carbon surface onto inner pore. As a previous theory, deposition firstly was initiated by surface adsorption in the outer surface. After surface adsorption, a bulky solution of activator has been fused by electrostatic interaction into covering surface formation. The deep deposition onto carbon framework was stimulated by a small atomic size of potassium which is less than 1 nm. It is logic if potassium particle has access to infiltrate the inner surface of the carbon. The potassium particle the aggregated in the inner pore and difficult to release during washing route. The aggregate of potassium has been solidified by the calcination process which is appeared by increasing mass after activation.

Figure 3. Spectra FTIR of Carbon Microsphere sampel

Fig 3 shows spectra FTIR of Carbon Microsphere sample. As can be seen in Fig 3.a-3.d, have similar functional group type such as OH group-type vibration stretch at peak 3500-3700 (cm⁻¹), acid group (OH) stretch vibration type at 2500-3300 (cm⁻¹), nitrile group (CN) vibration at 2100 to 2260 (cm⁻¹), Alkyne groups stretch vibration group (CO) stretch vibration at1670 to 1820 (cm⁻¹), ether groups at 1000-1300 (cm⁻¹) Amina cluster-type at 1080-1360 (cm⁻¹) Alkyl halide group at 1000-1400 (cm⁻¹) and halide ion (F, Cl, Br) at 600-500 (cm⁻¹) [20]. The interesting phenomenon observed in the AMC 25%
which shows the highest peak at the fundamental functional group and AMC 5% have the lowest peak. It is similar with our prediction before which is the high concentration of activator not only deposited onto inner carbon pore but also act as anchor sites to adsorption another molecule such H2O, acid, Carbonyl, Halide and hydroxyl from the free atmosphere. It is an urgent reason that explains why AMC 25% have greater functional group than another sample. In addition, all information on SEM and mass change have been confirmed by FTIR result. The influence of high functional group to the material character could be expressed by adsorption performance.

Fig 4 shows the results of adsorption of ibuprofen using UV-Vis at 272 nm taken every 5 minutes. of eas can be seen at Fig 4, the equilibrium state of AMC 5%, AMC 10%, AMC 15%, and AMC 20% are 25, 5, 15 and 35 min, respectively. It is implied that high activator concentration has a big impact not only to the increase surface area but also absorbed functional group during preparation. The amount of ibuprofen concentration (Ct) of AMC 5%, AMC 10%, AMC 15% and AMC 20% closely to 21.67, 17.17, 17.10, and 16.01 mg kg⁻¹. It is clearly shown that a high concentration of activator decrease adsorption concentration at the time due to the big destruction part.

Figure 5  Langmuir adsorption isotherm of AMC5%
**Table. 3 Adsorption Capacity ($q_{\text{max}}$) on AMC sample at variation activator concentration**

| [KOH] %/ν | Sample    | $Q_{\text{max}}$(Mg / g) |
|-----------|-----------|--------------------------|
| 5         | AMC-5%    | 55.90                    |
| 10        | AMC-10%   | 59.06                    |
| 15        | AMC-15%   | 59.21                    |
| 20        | AMC-20%   | 59.96                    |

Fig 5 shows the Langmuir adsorption isotherm of AMC5% which have linearity closely to the 0.9999. The table describes the relationship KOH concentration with a maximum adsorption capacity for MC to adsorption ibuprofen ($q_{\text{max}}$). We can see AMC 20% is highest adsorption performance which is imply that increasing surface area after activation process. In adsorption, not only pore and surface that give impact to the equilibrium or capacity but also a functional group of material. In our prediction, ibuprofen has a hydrophilic character on hydroxyl site in a double bond surface which has a great attraction to the hydrophilic material. The surface of AMC20% sample has been dominated by hydrophilic sites which are could increase the affinity between ibuprofen-carbon interaction. It is clearly different if we compared with AMC5% which has the highest adsorption capacity due to the natural hydrophobic character of the material.

4. Conclusion
Carbon microspheres have been successfully synthesized via templating method using Pluronic F127 triblock copolymers, gelatin, sucrose, and sulfuric acid. The step of synthesis involving hydrothermal reactor, the partial carbonization and pyrolysis under nitrogen flow followed by potassium hydroxide activation at room temperature for 24 hours using a variation of the activator concentration at 5, 10, 15 and 20 (% w / ν), respectively. Activated carbon microspheres were characterized by SEM and FTIR. In this study, it was found that the mass of carbon after activation increases due to deposition of potassium and free water molecules. Morphology of AMC sample as well as football-like structure with a pore size of 0.5 to 15 μm. The increasing concentration followed by increasing aggregation of impurities. FTIR results conclude that AMC sample dominated by OH, nitrile, C-C, carbonyl, and ether as a functional group. In this study it was found that increasing activator concentration have an impact on the high adsorption capacity due to the deposition impurities, increasing surface area and functional group enhancement.

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