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Synthesis of Mesoporous Carbon CMK-3 and CMK-5 Materials and Their Application for Drug Loading-Release System

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Abstract

The different structure of ordered mesoporous carbon CMK-3 and CMK-5 material was synthesized via a hard template route using SBA-15 and Al-SBA-15 as hard castings and sucrose as the carbon source. The first hard casting, mesoporous silica SBA-15 was synthesized via soft-templating route using block copolymer (P-123) as directing agent and tetraethoxysilane as the silica source. The second hard casting, mesoporous silica Al-SBA-15 was synthesized via incorporating route using SBA-15 as supporting material and Al_2O_3 as an aluminum precursor. Characterization of a mesoporous texture of the samples was investigated by X-ray diffraction, scanning electron microscopy and nitrogen adsorption-desorption techniques, and FTIR. The loading release performance of CMK-3 and CMK-5 was investigated by ibuprofen molecule as a drug model. We found that CMK-5 had a better loading capacity than CMK-3 as determined by their performance results in releasing ibuprofen in which the release rate of mesoporous structure of CMK-5 was slower than CMK-5 due to the power of anchor nanorod of carbon.

Keywords: mesoporous, carbonization, carbon, CMK-3, CMK-5, loading, release, ibuprofen

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1. Introduction

Ibuprofen is the most popular analgesic drug as an anti-inflammatory treatment in the medical and pharmaceutical area [1]. The unique character of ibuprofen; such as high activity, appropriate size and fast half-life; made this drug as one of the most popular drugs not only for human health but also for research development [2]. Ibuprofen is not only sustainable but also controllable for drug delivery system. For this reason, many attention and research have been directed for studying ibuprofen.

In ibuprofen research of drug delivery model, it was reported that the adsorption method is the most effective technique to remove this organic molecule drug as a pollutant in the aquatic area [3]. The previous report has been used activated carbon as adsorbent not only for ibuprofen but also for another organic pollutant [4]. However, activated carbon provides microporous part that made this adsorbent not accessible for the large molecule. It was challenging for ibuprofen that has a big size (1.0x1.5x0.8 nm3) to infiltrate onto activated carbon pore due to the limitation of the pore size [5]. This problem has been solved by mesoporous material which is discovered for the first time in 1992 by Exxon Mobil Oil Company [6].

Mesoporous material provides a large pore size which is favorable for any application that involves a big molecule. The mesoporous carbon material is the developed branch of mesoporous material that provides ordered structure, larger pore size, higher pore volume, larger surface area, tunable pore dimension and higher thermal and mechanic stability than conventional material [7-8]. The availability of the large pore of mesoporous carbon made the diffusion step during the adsorption process easier than conventional material. Mesoporous carbon has been used as an adsorbent for the bulky pollutant such as methylene blue, Red 31 and Black 5 [9]. The adsorption mechanism of pollutant onto mesoporous carbon was difficult to understand. Two of the most common mesoporous carbon materials that attract a considerable attention in the research field are CMK-3 and CMK-5. Both of them can be synthesized using exotemplating method [10]. CMK-3 is synthesized by using SBA-15 as a template but CMK-5 by using Al-SBA-15. The different character amongst them is an exciting point for further investigation. In the best of our knowledge, the investigation about ibuprofen adsorption onto CMK-3 and CMK-5 has been rarely done.

In this work, we focused on the synthesis and characterization of CMK-3 and CMK-5. CMK-3 and CMK-5 material was synthesized via a hard template route using SBA-15 and Al-SBA-15 as exotemplate and sucrose as the carbon source. Characterization of the mesoporous texture of the samples were performed by X-ray diffraction, scanning electron microscopy and nitrogen adsorption-desorption techniques, FTIR and element analysis. The loading capacity obtained from the adsorption mechanism onto CMK-3 and CMK-5 was examined using ibuprofen as a drug model.

2. Experimental

2.1. Materials

The soft template (Pluronic P123), the source of carbon (sucrose) and silica (TEOS), and the drug model (ibuprofen) were supplied by Sigma. The chemicals including hydrochloric acid, sulfuric acid, natrium hydroxide, aluminum chloride, and n-hexane were purchased from Aldrich.

2.2. Synthesis of exotemplate SBA-15 and Al-SBA-15

The soft template (P123) was mixed in hydrochloric acid by stirring at room temperature for 6 h. The resulting solution was added into the TEOS, followed by stirring at the same temperature for 24 h. The resulting solution was aged into the hydrothermal reactor at 100 °C for 24 h. The white powder was filtered by using a Whatmann paper and then washed with aquadest and dried at 100 °C for 24 h. The resulting powder was calcined at 550 °C for 8 h. The resulting sample of this procedure was labeled as SBA-15. Next, we made the mixture of SBA-15 and aluminum chloride in ethanol solution, followed by calcination to produce Al-SBA-15.

2.3. Synthesis of CMK-3 and CMK-5

SBA-15 was added into the sucrose solution (sucrose and sulfuric acid) followed by drying at 100 °C for 8 h and partial carbonization at 160 °C for 8 h. The brown powder was mixed with the half of sucrose solution then treated as the first step. Finally, the black resulting powder was carbonized at 900 °C for 8 h then washed with natrium hydroxide solution for removing SBA-15. The resulting black sample was labeled as CMK-3. For the synthesis of CMK-5, all procedure was similar to CMK-3 synthesis, but SBA-15 was replaced by Al-SBA-15

2.4. Characterization

The crystallinity of the material was analyzed by XRD (a Bruker D8-Advance powder diffractometer using Ni-filtered Cu-Ka radiation (k = 1.54056 Å) over a two theta range of 10–80. The three dimension and morphologies of material were characterized by an SEM (instrument (Philips CM30) operating at 10 kV in which each material was dispersed in absolute ethanol and then covered with perforated carbon film. The porosity and pore size was investigated by Nitrogen adsorption-desorption (Nove instrument) in which

each sample was degassed for 5 h at 305 °C before treatment. The functional group of each sample was analyzed by FTIR (Shimadzu 1400). The ibuprofen concentration after adsorption was measured by UV–Vis spectrophotometer (Shimadzu model V-670).

2.5. Ibuprofen adsorption

Ibuprofen was dissolved in hexane solution (10 b/v) followed by stirring at 15 °C for 2 h. The ibuprofen concentration at a range of 10-80 ppm was prepared to an obtained standard curve for calibration. The concentration of each variation was analyzed by UV–visible spectrophotometer at an absorbance wavelength of 262 nm.

3. Results and Discussion

Figure 1 shows the morphology and three dimension image of CMK-3 and CMK-5 observed by SEM. The aggregates of CMK-3 and CMK-5 as can be observed in SEM images show three dimension size of 0.5x3x10 μm^3 and 0.1x2x10 μm^3, respectively. The shape of CMK-3 was observed as a noodle-like structure but CMK-5 appeared as a bunch of noodle-like structure with overlapping parts in the whole surface. The CMK-3 morphology is similar to CMK-5 with small differences in mouth pore and overlapping sites. The overlapping sites in CMK-5 still showed the regular carbon rod as CMK-3 structure. However, the overlapping sites in CMK-5 strongly influenced the larger surface area due to microporous existence generated by the thousand small spaces between carbon walls. For small conclusion, both of CMK-3 and CMK-5 showed an ordered mesoporous structure without any significant destruction after the carbonization step.

Figure 2 shows the diffractogram of XRD in the wide 2θ region (10–50°). Mesoporous carbon CMK-3 and CMK-5 shows graphite structure at the reflection in 002 planes. As we can see, the broad peak from 2θ 15° until 30° represents the rod carbon of both CMK-3 and CMK-5. In particular, CMK-5 was graphitized higher than CMK-3 as can be observed in shifting peak phenomenon at 26.1° to 26.6°. It might occur due to aluminum ion that acted as a catalyst during carbonization section. For the comparison, the weak and broad peak of CMK-3 in 002 planes was a clear evidence of the smaller graphitic part in CMK-3. The XRD results describe the position of aluminum in Al-SBA-15 not only for the exotemplate part but also as the important catalyst for producing high graphitic structure of CMK-5. For a sum of all, both CMK-3 and CMK-5 has been successfully synthesized by an exotemplating method with a different graphitic percentage.

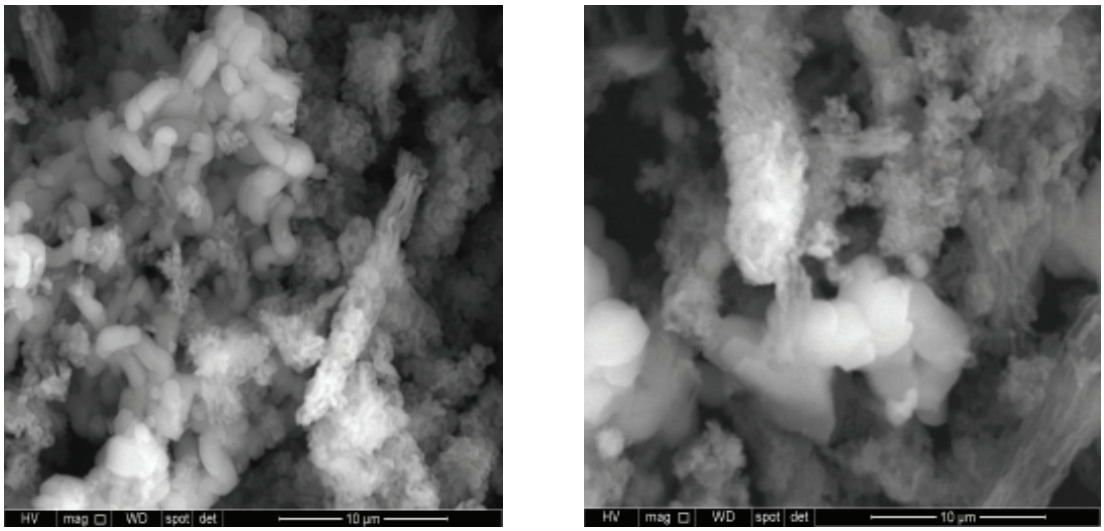

Figure 1: Morphology of (A) CMK-3 and (B) CMK-5 analyzed by SEM.

Figure 3 shows the isotherms curve of CMK-3 and CMK-5 obtained by nitrogen adsorption-desorption. The isotherms curve shows the type IV (Hysteresis loop H-1) which represents the mesoporous pore type of CMK-3 and CMK-5. The isotherm parts not only clearly describe the mesoporous existence but also the ordered structure of CMK-3 and CMK-5. The surface area of CMK-5 (450 m^2/g) was higher than CMK-3 (450 m^2/g) due to the micropores existence between the double carbon walls of CMK-5. The double carbon walls of CMK-5 were generated by aluminum ion position as the anchor point of carbon during its synthesis. The diameter of CMK-3 and CMK-5 are 4.4 nm and 3.5 nm, respectively. This information represents that the pore of CMK-5 (or in the other word, the space of CMK-5 between each carbon wall) is smaller than that in CMK-3 due to the double carbon walls built in CMK-5. As can be seen in Figure 2, the second prediction about the smaller size of CMK-5 is appeared by the shrinkage process during carbonization. As the summary, the differences of the resulting pore of CMK-3 and CMK-5 were strongly affected by the differences of exotemplate species.

Figure 4 shows the FTIR spectra of CMK-3 and CMK-5. The functional groups of CMK-3 and CMK-5 as can be seen from the FTIR show similar peaks at 1740 cm^{-1}, 1250 cm^{-1}, and 1100 cm^{-1} that represent to C–O–C stretching, CH2 stretching and C=C bending mode. These peaks were related to carbonyl, carbene, butanol, and butane that indicated the carbon and graphite character. From the FTIR spectra, the peaks of double carbon bond on CMK-5 can seem higher than that in CMK-3 at peak 1470 cm^{-1}, 1260 cm^{-1}, 1170 cm^{-1} and 1150 cm^{-1} which indicated that CMK-5 graphite structure was strongly higher than CMK-3. As our prediction, aluminum ion on SBA-15 template acted as a catalyst as well as an anchor point which increased the graphite peak not only as

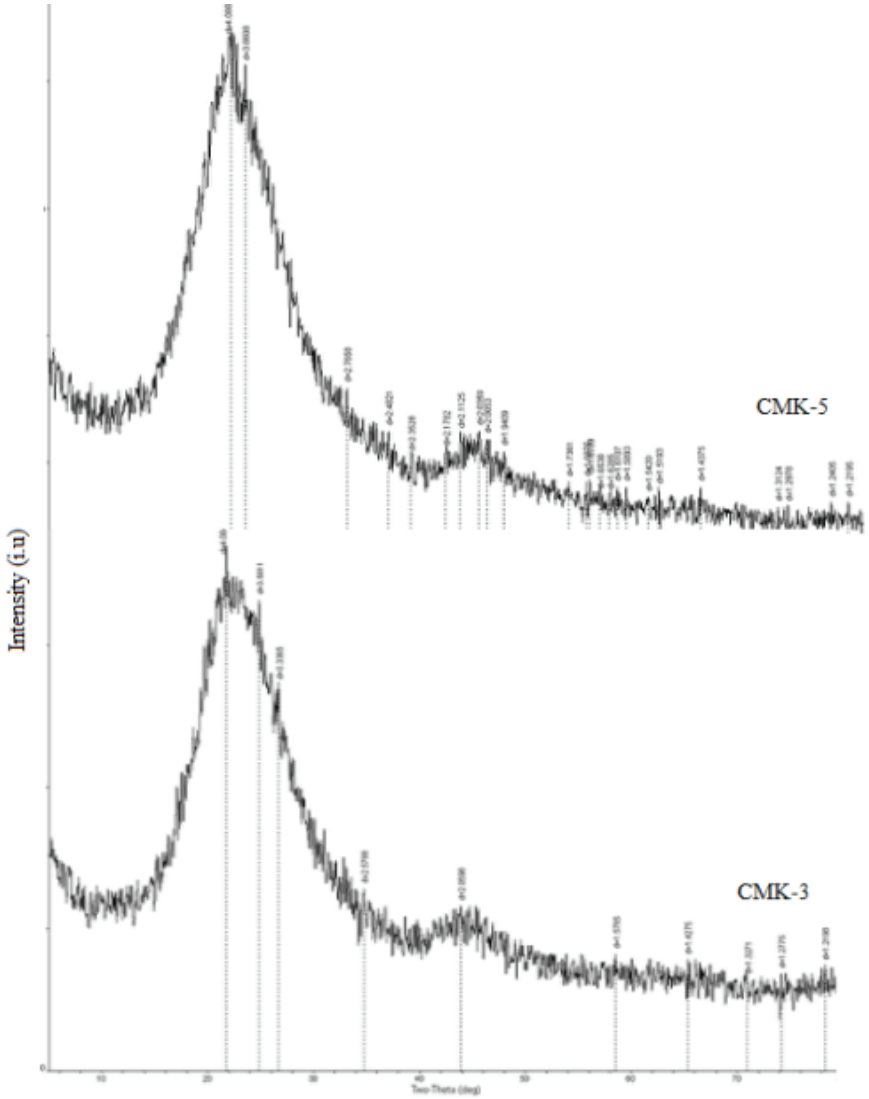

Figure 2: Diffractogram of CMK-3 and CMK-5 analyzed by XRD.

can be seen at FTIR but also on the XRD pattern. From all characterization results, it can be concluded that CMK-5 had higher textural character than CMK-3 but contained a small overlap space which was generated by aluminum ion on Al-SBA-15 template.

Figure 5 shows ibuprofen adsorption using CMK-3 and CMK-5. The experiment was carried out up to 100 min. As can be seen at Figure 5, both of CMK-3 and CMK-5 reach an equilibrium point with the adsorption rate of 95% at the first 45 min then followed by a constant adsorption rate thereafter. CMK-5 absorbed up to 150 mg/g ibuprofen and CMK-3 up to 125 mg/g at equilibrium condition. The adsorption capacity of CMK-5 was higher than CMK-3 and this was attributed to the high surface area of CMK-5. The other prediction is that a large number of spaces which were generated by the overlapping sites in CMK-5 enhanced the ibuprofen diffusion. Ibuprofen that infiltrates onto CMK-5 was deposited in the inner pore which is resulting in the higher adsorption capacity.

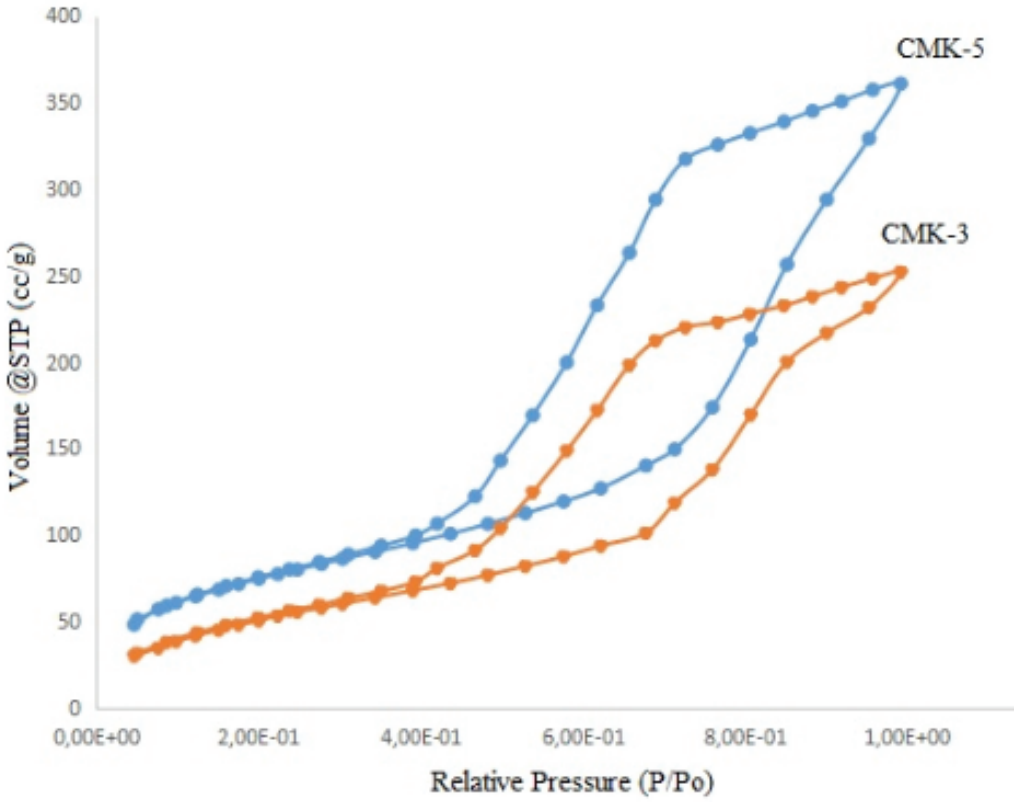

Figure 3: Isotherm adsorption of CMK-3 and CMK-5 analyzed by Nitrogen adsorption-desorption.

After ibuprofen adsorption, CMK-3 and CMK-5 were released by SBF solution. The result is not shown here but it informs that the releasing power of CMK-3 is higher than CMK-5. The releasing power of CMK-3 may be attributed to a large number of mesoporous sites that easier leach ibuprofen from the framework. The releasing power of CMK-5 may be attributed to a large number of mesoporous sites that ease the leakage of ibuprofen from the framework. The large number of micro spaces of CMK-5 have been successfully generated by the aluminum site at Al-SBA-15 which increases the character and the adsorption performance of CMK-5 in overall.

4. Conclusion

Our work presented a comparison study between mesoporous carbon CMK-3 and CMK-5 as a drug adsorbent. The major structure of both CMK-3 and CMK-5 was graphite without any significant impurities. The result of this study shows that CMK-5 has higher textural character than CMK-3. The adsorption capacity of CMK-3 and CMK-5 are 125 and 147 mg/g. So from this study, we can conclude that CMK-5 is the best potential material if compared with the textual properties and the adsorption performance of CMK-3. The

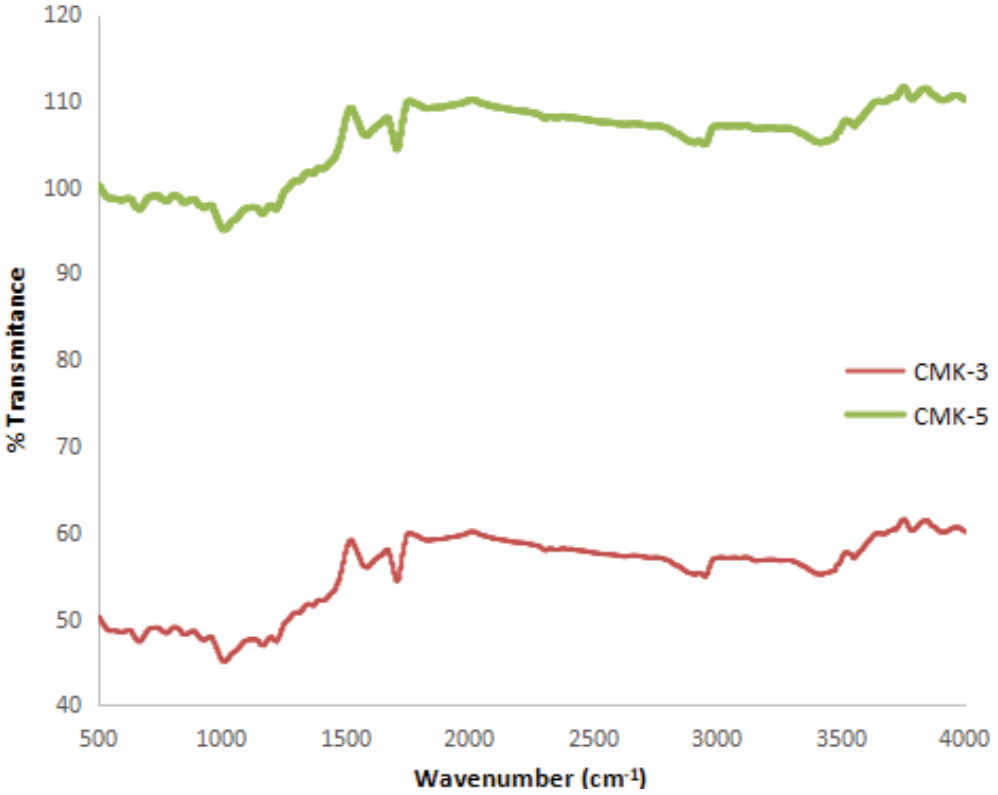

Figure 4: Spectra of CMK-3 and CMK-5 analyzed by FTIR.

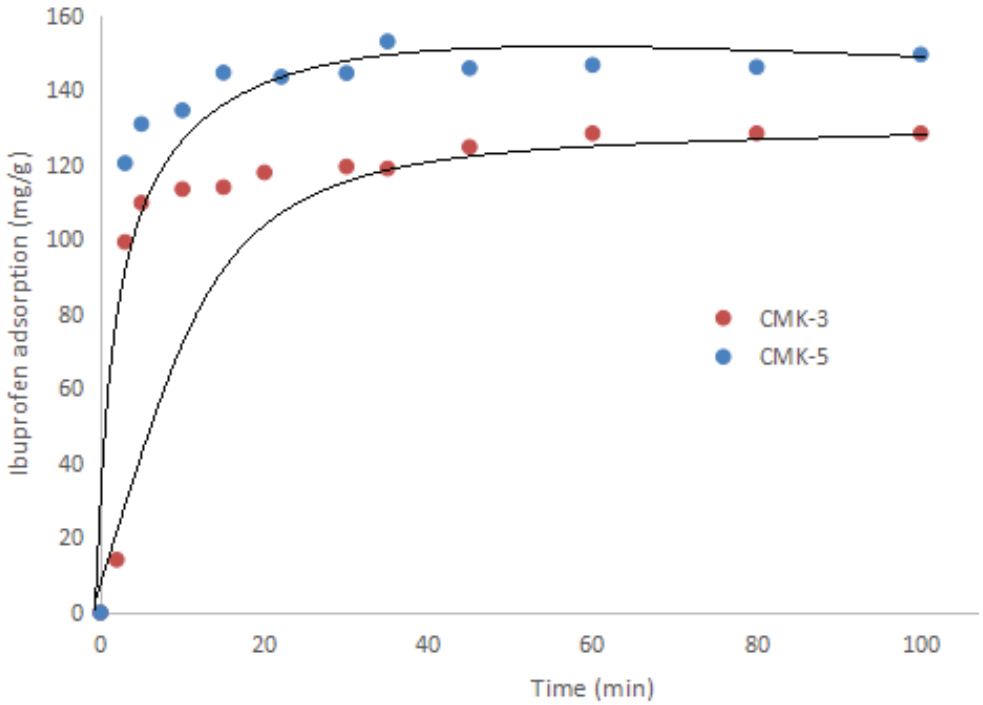

Figure 5: Adsorption plot of CMK-3 and CMK-5 using ibuprofen as adsorbate.

release rate of CMK-3 is faster than CMK-5 due to a large number of mesoporous sites. The large surface area and ordered structure is the best reason for higher ibuprofen

adsorption. The high surface area of CMK-3 and CMK-5 was generated by the exotemplating effect which is increased in CMK-5 sample due the aluminum site as a catalyst. This study concludes that CMK-3 and CMK-5 is a potential material for drug delivery system

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