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Effects of acidity on the mesoporous carbon CMK-3 structure during Ibuprofen molecule adsorption

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Abstract A novel molecular sieve based mesoporous Carbon CMK-3 as adsorbent were prepared by hard templating method using sucrose and mesoporous silica SBA-15 as source of carbon and nanocast, respectively. The impregnation sequence of sucrose onto SBA-15 catalysed by sulphuric acid and followed by pyrolysis process at 900°C for 6 h. The mesoporous Carbon CMK-3 adsorbent were characterized by (Fourier transform infrared spectrometer) FTIR, scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) techniques. The effects of acidity on ibuprofen adsorption performance were investigated using UV-Vis. The result shows that there was a strong effect between acidity condition and adsorption performance. The high acidity condition did not change the big part of mesoporous Carbon CMK-3 microstructure. The shrinkage of mesoporous carbon CMK-3 structure showed a better yield of total ibuprofen adsorbed which reached loading degree up to 65 (%wt).

Keywords: mesoporous carbon CMK-3, ibuprofen, adsorption, acidity, structure

1. Introduction

Mesoporous carbon CMK-3 have attracted attention as smart material in host-guest chemistry due to their unique uniform feature complete with high surface areas, high pore volume and extremely high mechanic and thermal stability [1]. The large mesoporous part on CMK-3 was accessible for big size of organic molecule in many application such as adsorption, drug delivery process, catalysis, capacitor, electrical storage and batteries [2]. Ordered mesoporous carbon CMK-3 has been recently started to propose as drug delivery material due to its large surface area for drug molecule accumulation using adsorption model for simulation [3]. However, the appropriate adsorption condition to optimize drug molecule adsorption using mesoporous carbon CMK-3 have been rarely investigated before.

One of the most popular anti-inflammatory drug in pharmaceutical area is ibuprofen which is called 2-[4-(2-Methylpropyl) phenyl]propionic acid [4]. Ibuprofen dimensions size is 1.36x0.74x0.52 nm³ which is big molecule categories need supporting material to access for any application [5]. The release of ibuprofen from drug industry or human excretion in aquatic life was destructed the balancing system. The simple solution to remove ibuprofen from water to save aquatic area is adsorption treatment. The previous researcher was report about the big potential for interaction between hydroxyl groups at the silica surface with ibuprofen through the hydrogen bonding [6, 7]. This interaction was claimed to decrease ibuprofen concentration in water environment [8-10]. However, the using of mesoporous carbon CMK-3 to remove ibuprofen from aquatic area rarely done. The improvement of adsorption



capacity was depended on the factor including acidity, character of functional group, adsorbent surface area, pore volume of adsorbent, weight of adsorbent and temperature.

This paper investigated the acidity factor in ibuprofen adsorption. Mesoporous carbon CMK-3 synthesized using mesoporous silica SBA-15 as hard template. The textural properties of mesoporous carbon CMK-3 analysed by FTIR, scanning electron microscopy and EDX. The acidity factor was carried out during ibuprofen adsorption at pH 1 and pH 3. Mesoporous carbon CMK capacity investigated by analysing the ibuprofen adsorption kinetics can lead to establish the use of this material for removal ibuprofen from aquatic purposes

2. Experimental

2.1. Materials

Ibuprofen was purchased from Sigma–Aldrich (>98% purity). Tetraethoxysilane was purchased from Eland Corporation. Sucrose, Acetic acid, hydrochloric acid, and sodium hydroxide were purchased from Sigma–Aldrich Company. All chemicals and reagents are of analytical grade and used without any further purification.

2.2. Synthesis of mesoporous carbon CMK-3

First, we have to synthesis mesoporous silica SBA-15 as hard template to synthesis CMK-3. SBA-15 mesoporous silica was prepared by using the triblock copolymer Pluronic P123, as a template. Pluronic P123 6.53 mmol was dissolved in a mixture of 10 ml distilled water and 1 ml HCl solution (37 wt%) at 35°C for 2 h with stirring. Tetraethoxysilane was added to the solution and stirred at room temperature for 24 h. The mixture was transferred to Teflon bottle and then heated at 100°C in an oven for 24 h. The white precipitate was filtrated then followed by washed using distilled water until neutral and then dried overnight in an air oven at 100°C. The sample yield then calcined by furnace at 550°C for 5 h. Mesoporous carbon CMK-3 was synthesized by adding SBA-15 to the stirring solution containing sucrose and sulphuric acid followed by drying at 100°C for 6 h and then carbonized at 160°C 6 h. The resulting black-brown powder was by 30% w/w sucrose solution. The sample was carbonized under pure nitrogen atmosphere in furnace at 900°C at a for 6 h. After SBA-15 removal by natrium hydroxide 2M, the resulting carbon washed and labelled as CMK-3

2.3. Textural and chemical characterization of activated carbons

The surface of activated carbons was characterized by FTIR using a Thermo Scientific Nicolet iS10 spectrometer equipped with a germanium crystal. A KBr detector was used for detection and the incident angle. All spectra were collected in the infrared region about 500–4000 cm^{-1} with any a spectral resolution. The morphologies of SBA-15 and carbon replica materials were observed by scanning electron microscope (SEM, JSM-7001F, JEOL) at a 2 or 5 kV accelerating voltage and elemental analysis observed by EDX

2.4. Ibuprofen Loading

The effect of acidity during ibuprofen adsorption was determined at pH 1 and pH 3. The ibuprofen solution with known concentration (100 ppm) was mixed by 20 mg mesoporous carbon CMK-3 then added by HCl 0.1M drop by drop until the whole solution reach pH 1 and pH 3. After mixed for 30 min, filtrate was separate from mixture at 5,10,15, 20, 25, 30, 35, 40, 45, 50, 55 and 70 min. The ibuprofen solution was analysed by UV-Vis (Shimadzu 650) to measure absorbance at wavenumber 262 nm. The concentration of sample and measured absorbance was to investigated the kinetic performance of ibuprofen onto CMK-3 in different acidity condition.

3. Result and Discussion

Fig. 1 shows the XRD patterns for mesoporous carbon CMK-3 in the wide 2θ region (5–80°). The reflections from all the samples are indexed to the 100, 110, and 200 reflections of the space group

p6mm. Fig. 1 shows a clear 200 reflection associated with the graphitic structure. These results imply that the carboneous rods in CMK-3-M were partially graphitized by the heating treatment. Based on the reference for typical graphite material, the 002 peak position for mesoporous carbon CMK-3 after ibuprofen adsorption at pH 3 was slightly shifted to a lower angle from 26.1° to 26.6° as same as previous result according to the Mbileni *et al.* [3]. For comparison, the peak position for mesoporous carbon CMK-3 after ibuprofen adsorption at pH 1 (curve not shown) still remain the original CMK-3 which is imply that low acidity not significant give impact for CMK-3 structure. This phenomenon was occurred by the covering domain by ibuprofen after adsorption. There is a change small part of CMK-3 after covering process. However, XRD result conclude that the graphitic of CMK-3 structure after ibuprofen adsorption of mesoporous carbon still stable without any significant destruction both in pH 1 and pH 3.

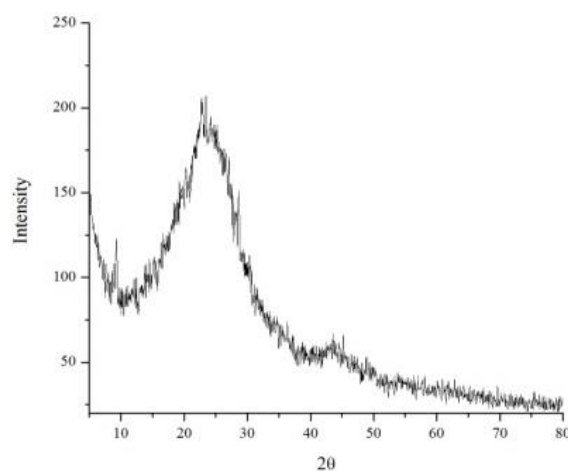


Figure 1. Diffractogram XRD of mesoporous carbon CMK-3 after ibuprofen adsorption at pH 3

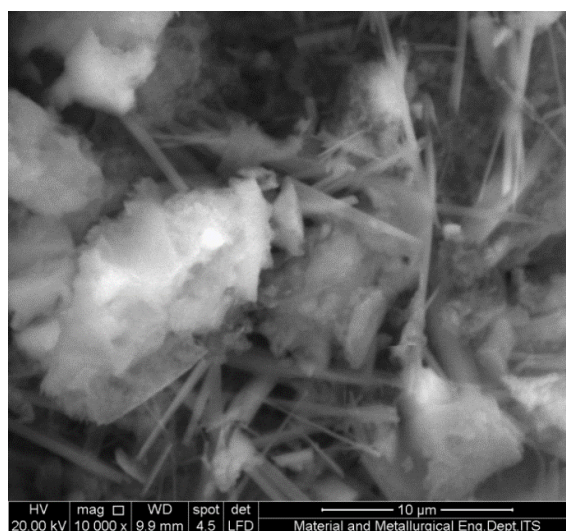


Figure 2. Scanning electron microscopy (SEM) of mesoporous carbon CMK-3 after ibuprofen adsorption at pH 3.

Fig. 2 shows scanning electron microscopy (SEM) observations which is revealed that the particle shape in mesoporous carbon CMK-3 were ribbon sheet-like which is size length were 5-10 μm with size

diameter 0.1–1.5 μm . The morphologies and sizes of mesoporous carbon CMK-3 were almost without changed if compare with SBA-15 (not shown). If we compare with CMK-3 after ibuprofen adsorption in pH1 (SEM not shown), the covering ibuprofen in CMK-3 surface at pH 3 larger than pH 1 which is imply that high acidity increased the bonding of CMK-3 and ibuprofen via hydrogen bonding (described in FTIR). The SEM results indicate that the mesoporous carbon CMK-3 materials covered by ibuprofen. Based on the ibuprofen size about $1.36 \times 0.74 \times 0.52 \text{ nm}^3$, it is logic if not all of ibuprofen adsorbed onto mesoporous carbon CMK-3 pore due to the agglomeration of big structure of ibuprofen on the mouth of CMK-3 pore. In particular, ibuprofen strongly promoted blocking pore the small part of mesoporous carbon CMK-3 but not significant to change the whole part of CMK-3 structure.

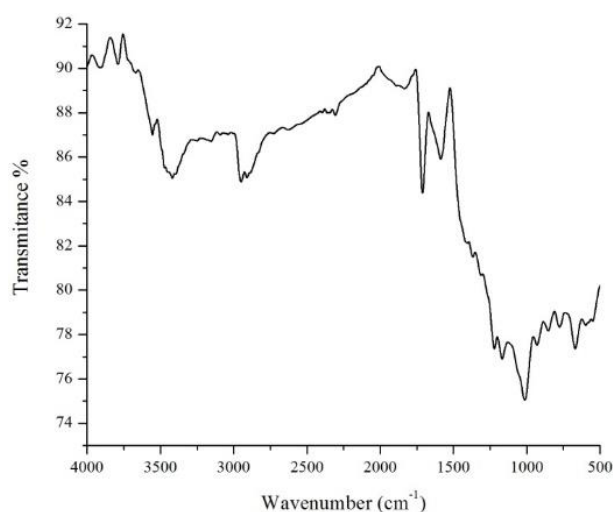


Figure 3. spectra FTIR of mesoporous carbon CMK-3 after ibuprofen adsorption at pH 3.

Fig 3 shows the FTIR spectra after loading ibuprofen at pH 3. The peaks at 802 and 1083 cm^{-1} in CMK-3 Spectra are attributed to the C-O symmetrical and asymmetrical stretching of carbon. these peak shows that graphitic part was more dominate than other structure. The O-H bond was observed in 3383-3500 cm^{-1} which is imply that CMK-3 structure at pH 3 have rich of hydrogen bonding. The peak of O-H bond in CMK-3 at pH 3 larger that at pH 1(Spectra not shown) which is imply that high acidity condition increasing the O-H bond. The hydrogen boding as our prediction act as the bond between CMK-3 and ibuprofen. The peaks at 1589 cm^{-1} , 1485 cm^{-1} , 1456 cm^{-1} and 1384 cm^{-1} in the pattern of ibuprofen are attributed to the frame vibration of benzene ring and carbonyl sites as the character of ibuprofen functional group. This phenomenon was suggested that ibuprofen was successfully loaded into the CMK-3 pore and. adsorbed into the deep carbon structure.

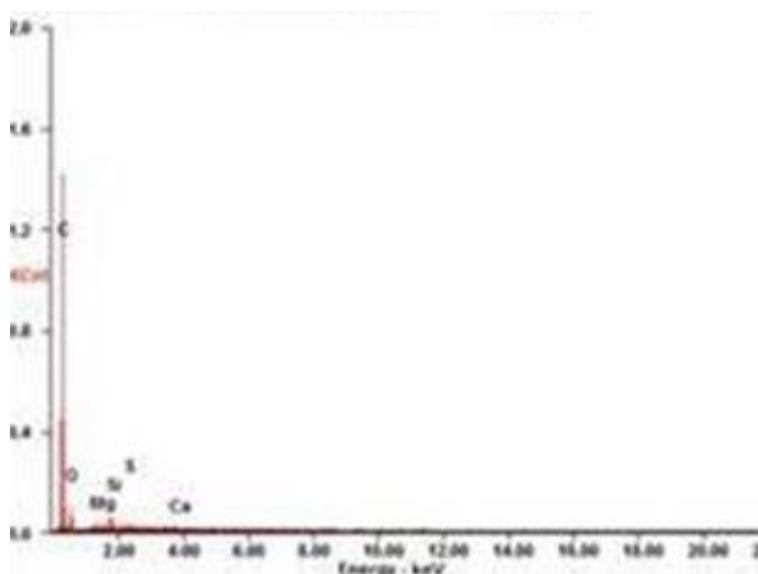


Figure 4. Elemental spectrum of mesoporous carbon CMK-3 by EDX after ibuprofen adsorption at pH 3.

Fig 4 shows the elemental analysis result by EDX. As can be seen in Fig 4, the composition of mesoporous carbon CMK-3 was dominated by carbon. The other element is silica, sulphur, magnesium, oxygen and calcium. The incomplete replication process from mesoporous silica SBA-15 to mesoporous silica CMK-3 give impact to the silica existence in final product. The emergence of magnesium, calcium and sulphur element in EDX spectrum was owing to the fact that the samples were have impurities during preparation. Based on the whole characterization result, CMK-3 structure of was successfully synthesized with graphitic type and ribbon-sheet like structure.

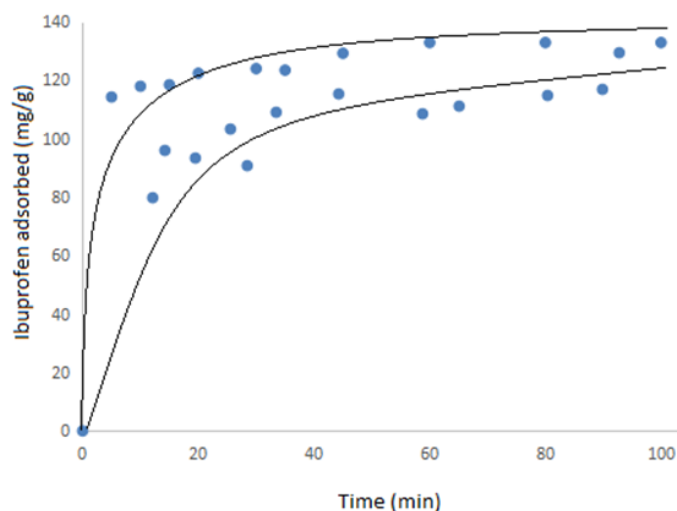


Figure 5. Plot of adsorption of Ibuprofen on mesoporous carbon at pH 1 (below) and pH 3 (above).

From all of the characterization result, we can see that the textural a structural properties of CMK-3 at pH3 is better than pH1. We have try to correlate this phenomenon with the trend of ibuprofen kinetic performance. Fig 5 shows ibuprofen adsorption experiments were carried out at pH 1 and pH 3 for 100 min. This study has an aim to investigate the acidity dependency of the ibuprofen adsorption capacity. The equilibrium models using the pseudo second order were analysed which is at pH 3, it gives the best

adjusted- $R^2=0.998$. the adsorption result suggests that the intra particle diffusion was consistent with the experimental kinetics at pH 3. The intra particle diffusion plot of the adsorption of ibuprofen on the mesoporous carbon at room temperature indicating three step. First, spontaneous adsorption of ibuprofen on the outer surface of CMK-3. Second, the intra particle diffusion was control the ibuprofen adsorption rate. The last stages show the end of the diffusion which was described by the slow rate of adsorption. The partially sum was concluded that the increasing time followed by the decreasing adsorption rate due to the limited intra particle diffusion rate. The adsorption kinetic of ibuprofen is faster at pH 3 than at pH 1 could be explained by a surface of mesoporous carbon CMK-3 surface repelling the functional group of ibuprofen in increasing pH solution. The adsorption of the ibuprofen at high pH has been only promoted by repulsive interactions. The increasing of repulsive interaction was affected by increasing interaction between ibuprofen and mesoporous carbon surface due to the increasing pH solution. Fig 5 showed a better yield of total ibuprofen adsorbed which reached loading degree up to 65 (%wt) with adsorption capacity 120 mg/g in the first 60 min. The high ibuprofen adsorption performance was similar with the high textural and structural properties of CMK-3 at pH 3. For the future, this result could be the urgent information for drug delivery system development due to the appropriate acidity condition for the high adsorption capacity material.

4. Conclusions

In this paper, mesoporous carbon CMK-3 was synthesized using SBA-15 as templates. The XRD, SEM images and FTIR spectra show that mesoporous carbon CMK-3 has ribbon sheet-like structure with size 0,1-10 μm which is dominated by carbon element with graphitic structure. Adsorption investigation at pH 3 show that mesoporous carbon CMK-3 could remove ibuprofen from aquatic better than pH 1. Mesoporous carbon CMK-3 at high acidity solution have better performance in kinetic adsorption and structural performance than low acidity with an adsorption capacity of 120mg/g and loading degree 65%. The high adsorption performance of mesoporous carbon CMK-3 at high acidity condition could be good information for ibuprofen removal large scale treatment in natural water resources

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