

Preparation and Characterization of Carbonized Material from Al-Fe-Mg-Si Nanocomposites Impregnated Biomass

Jin Woo Kim¹, Chul Jae Lee²

¹Department of Chemical Engineering, ChungBuk National University,

²School of Chemical Industry, Yeungnam College of Science & Technology

E-mail: kjw8613@naver.com, cjlee@ync.ac.kr

Abstract

Our present study, we impregnated Al-Fe-Mg-Si (NFM) nanocomposites having various concentrations 0, 1000, 3000, and 5000 mg/L in biomass in order to make carbonized biomass. We characterized the properties of the impregnated samples through thermogravimetric/differential thermal analysis (TG-DTA), pore distribution, scanning electron microscopy (SEM). The best results were observed for a NFM nanocomposites concentration of 5000 mg/L. After the first heat treatment, carbonization, and activation processes, the fixed carbon ratio and iodine adsorptivity were increased by 21.89% and 368 mg/g, 23.98% and 475 mg/g, 26.40% and 238 mg/g, respectively. The remove rate of malodorous and VOCs were that the sample shows good removal capabilities. From above results, our sample could be used for the removal of noxious and malodorous gases and for the purification of wastewater.

Keywords: Biomass, Nanocomposites, Impregnation, VOCs.

1. Introduction

Biomass burning is a significant source of atmospheric gases and particles. It occurs naturally in wildfires and is also employed by over half the world population for cooking, land clearing, heating, lighting, and other uses [1]. However, biomass burning emissions strongly affect regional air quality, and can be transported over large distances to impact regions distant from the source [2–5].

Environment pollution problems have currently attracted increasing public concern with the development of industrialization and urbanization. Especially, the emission of volatile organic compounds (VOCs) released from industry and automobiles to atmosphere are a growing public concern as most VOCs contaminate environment. In some cases, conventional techniques like adsorption, combustion and condensation are unsuitable for application [6–8].

Also, nanomaterial based adsorbents have been studied extensively and showed much faster rates and higher efficiency toward pollutants as compared with the conventional adsorbents [9–13]. Various carbonaceous nanomaterial have been adopted as adsorbents for the removal of organic pollutants such as graphene [10] mesoporous carbon [12], nano-titanium dioxide [13], and carbon aerogels [14]. Among them, carbon aerogels were considered as one of the cost-effective carbon materials for water decontamination due to their low cost and excellent capability.

Manuscript received: June 20, 2018 / revised: June 21, 2018 / Accepted: June 22, 2018

Corresponding Author: cjlee@ync.ac.kr

Tel: +82-53-650-9277, Fax: +82-53-625-5070

School of Chemical Industry, Yeungnam College of Science & Technology

Our previous study was that we developed a method using residual metals to manufacture functionally activated carbon materials economically [15] and carried out after-treatments of metals such as Ag, Cu, and Ni with activated carbon and studied their adsorption, pore, surface, and antibiosis properties. We found that when carrying out treatments using the activated structure, the metals affected the properties of the pore and played a harmful role as active materials [16].

In this study, we impregnated the NFM nanocomposites in biomass, and this in turn was incorporated into the carbon matrix. The biomass-impregnated NFM nanocomposites showed improved yield, increased adsorptivity and deodorization with the carbon content.

2. Experimental process

2.1 Biomass

Platycarya strobilacea branches that were crushed using a 5~14 mesh and dried until the moisture content was less than 5 wt. % were used as biomass samples.

2.2 Al-Fe-Mg-Si (NFM) nanocomposites

We prepared NFM nanocomposites having concentrations of 1000, 3000, and 5000 ppm by the micelle method and by dilution using distilled water. The molar ratio of the aluminum, iron and magnesium nano particle is 1:4.6:2.3, respectively. The pH of the diluted NFM nanocomposites solution is 2.38. Moreover, using a nanoparticle size analyzer (NANOPHOX NX0046), the average particle size was found to be 7.42 nm.

2.3 Pore distribution analysis of impregnated nanocomposites sample

We used a Mercury Porosimeter (Micromeritics, Model: Auto Pore IV 9520) to analyze the pore distribution of the impregnated nanocomposites sample.

2.4 Analysis of physical properties

The proximate analysis was used the KS 1082 to test and investigate the moisture content of the sample, along with the fixed carbon ratio, hardness, packing density, pH, loss on drying, and ash content. Also, the thermo gravimetric analysis was used the Mettler Toledo TGA851 to conduct the heat analysis. During pyrolysis, the sample temperature was increased from 30 to 600 °C at a rate of 10 °C/min.

2.5 Sample preparation

We dried the Platycarya strobilacea branches sample at 100 °C for 8 hr until the moisture content was less than 5 wt. % and then, used the micelle method to impregnate the NFM nanocomposites into the sample with a volume ration of 1:1.6. During impregnation, the sample was maintained at 40 °C for 120 min, following which it was dried using a drier at 120 °C for 8 h until the moisture content was less than 5 wt. %.

In the first heat treatment process of the impregnated NFM nanocomposites was that the 100 g of the impregnated NFM nanocomposites was heated from room temperature to 350 °C at a rate of 5 °C /min under a 500 cm³/min flow of a 1:1 mixture of air and N₂. The sample was then maintained at 350 °C for 2 hr. We measured the physical properties of the treated samples from the iodine adsorptivity, fixed carbon ratio, and

ash content. Carbonization process of the impregnated sample was that the sample temperature was then increased to 600 °C at the same rate under N₂ atmosphere and maintained for 2 hr. The analysis of physical properties was again similarly. Finally, the activation process, the temperature of the carbonized sample (10 g) was increased to 900 °C at the same rate under N₂ atmosphere with an additional 400 cm³/min flow of CO₂. The sample was activated for 2 hr, and its physical properties were again measured in the same process.

3. Results and discussion

In order to manufacture highly functional nanocomposites, it is necessary to disperse the impregnated substances and uniformly functionalize the pores and surface of the biomass. In doing so, it is important to consider the particle size; even though their size is small, the particles can confer various functionalities because they have a large specific surface area.

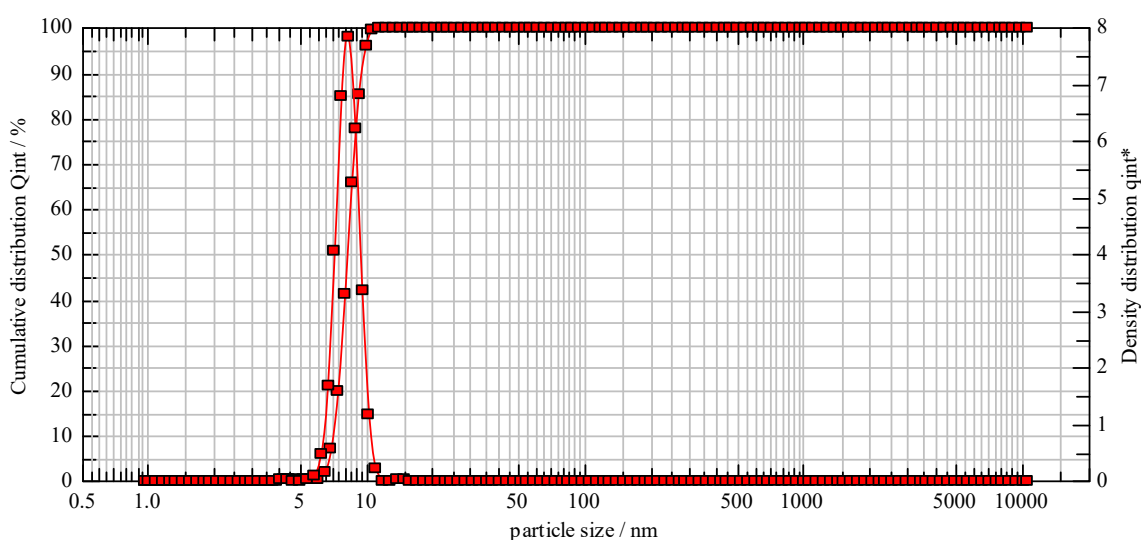


Figure 1. Analysis for particle-size distribution of NFM nanocomposites.

Figure 1 shows the analysis for particle-size distribution of NFM nanocomposites. The average particle size is 7.42 nm. The solution ratio of sample to impregnation is based on situations without residual solutions after the impregnated solution is completely absorbed in the sample. When the impregnation temperature is less than 40 °C, the impregnation time increases, whereas when it is higher (70 °C), the time decreases. The impregnation temperature and time did not change with impregnation concentration. The optimal conditions were found to be an impregnation temperature and time of 40 °C and 2 hr, respectively, and a sample to solution ratio (wt. %) of 1:1.2. The surface of the nanoparticle-impregnated sample was measured by SEM and by observing the pore distributions. Figure 2 shows the analysis of the pore distribution revealed a change in the pore size, and with an increase in the concentration of the impregnated NFM nanocomposites from 1000, 3000 and 5000 mg/L, the pore size reduced from 100 μm to 10 μm. Figure 3 shows differential thermo gravimetric (DTG) results of 0 mg/L, 1000 mg/L, 3000 mg/L and 5000 mg/L of NFM nanocomposites. The 0 and 1000 mg/L of NFM nanocomposites were dried by heating it to 180 °C, following which the volatile components were rapidly pyrolyzed by increasing the temperature from 330 to 380 °C. Also, The 3000 and 5000 mg/L of NFM nanocomposites were dried by heating it to 180 °C, following which the volatile components were rapidly pyrolyzed by increasing the temperature from 280 to 370 °C.

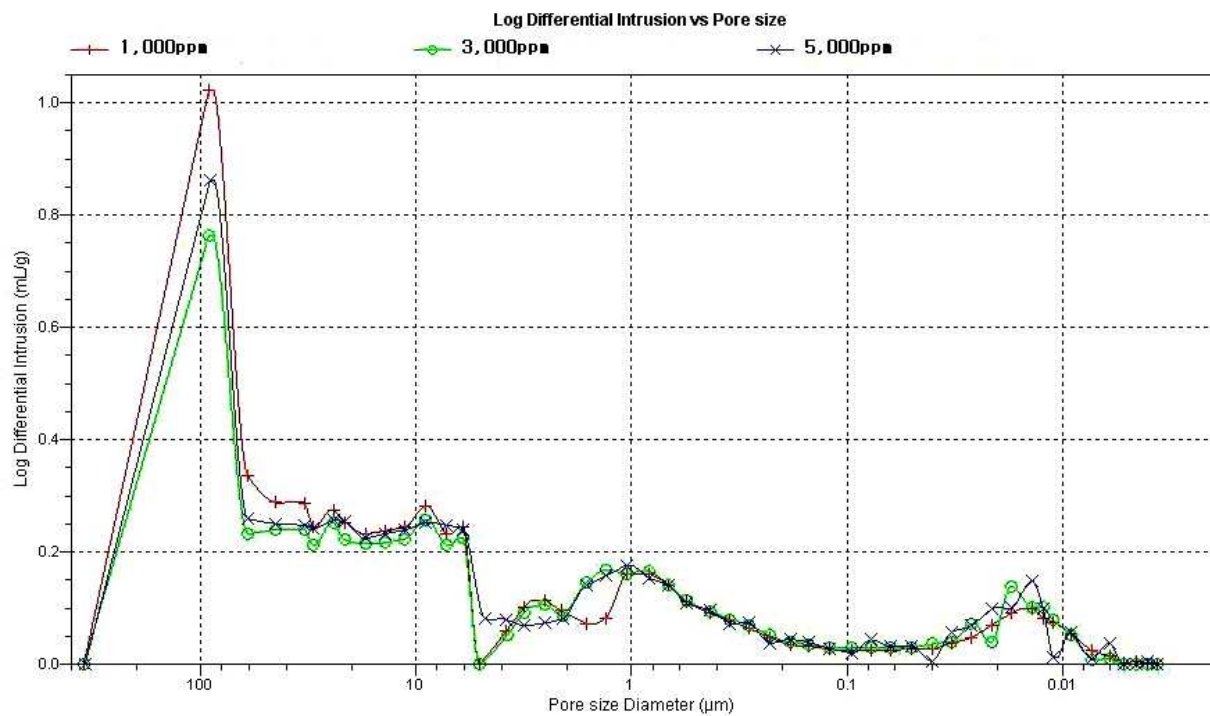


Figure 2. Pore distribution curves of 1000mg/L, 3000mg/L and 5000mg/L of NFM nanocomposites.

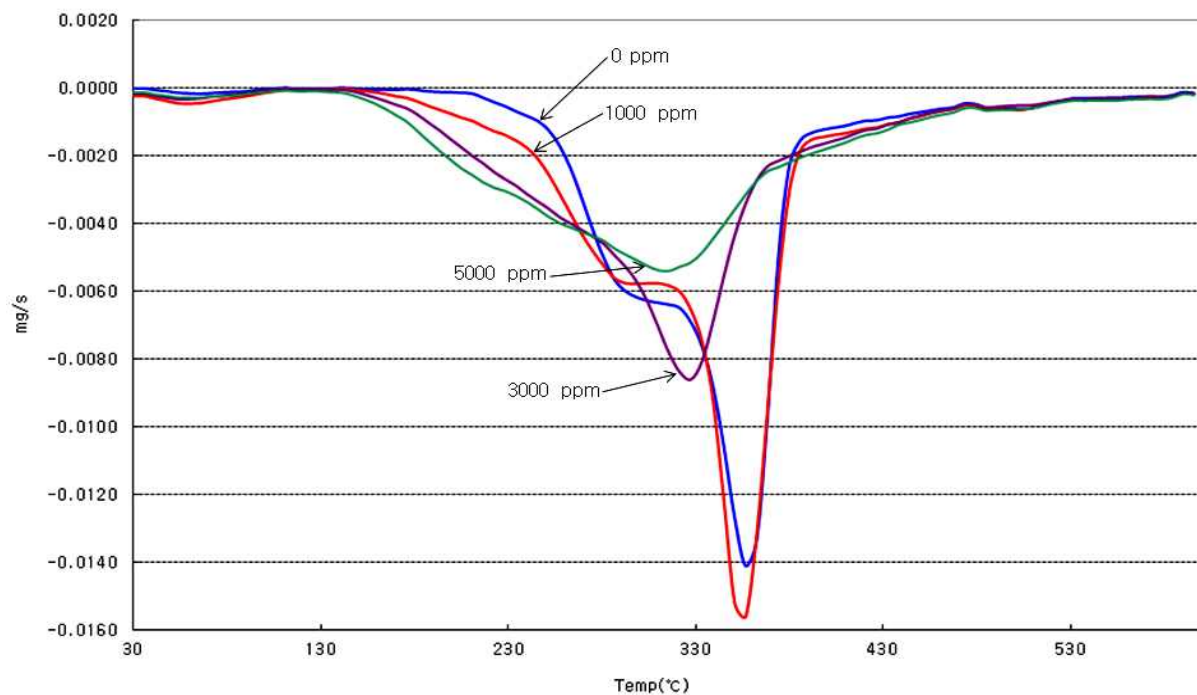


Figure 3. DTG curves of 0 mg/L, 1000 mg/L, 3000 mg/L and 5000 mg/L of NFM nanocomposites.

From above results, we identified that the pyrolytic temperature gradually decreased with an increase in the

impregnation concentration; the lowest temperature was 371.8 °C for the 0 mg/L of NFM nanocomposites, but it reduced to 319.2 °C for a 5000 mg/L of NFM nanocomposites. Therefore, we confirmed that the change in the lowest temperature was attributable to the varying speed of heat transfer depending on the impregnation concentration, which in turn arose from the difference in the speed of heat transfer inside and outside the NFM nanocomposites [17, 18].

Table 1. Change in fixed carbon ratio and iodine adsorptivity with impregnation of NFM nanocomposites during heat treatments at 350 °C and 600 °C for 2 hr.

| Impregnation of NFM nanocomposites (mg/L) | Heat treatments (°C) | Fixed carbon (%) | Iodine adsorption (mg/g) |
|---|----------------------|------------------|--------------------------|
| 0 | 350 | 31.48 | 200 |
| | 600 | 20.05 | 300 |
| 1000 | 350 | 32.59 | 206 |
| | 600 | 21.89 | 368 |
| 3000 | 350 | 35.31 | 221 |
| | 600 | 23.98 | 475 |
| 5000 | 350 | 37.64 | 238 |
| | 600 | 26.40 | 534 |

Table 1 shows the fixed carbon ratio and iodine adsorptivity during the first heat treatment and carbonization processes. During the first heat treatment (350 °C / 2 hr), with an increase in the impregnation concentration of NFM nanocomposites from 0 to 5000 ppm, the fixed carbon ratio increased from 31.48% to 37.64%, and the iodine adsorption, from 200 mg/g to 238 mg/g. Similarly, during carbonization (600 °C / 2 hr), the fixed carbon ratio increased from 20.05% to 26.40%, and the iodine adsorption, from 300 mg/g to 534 mg/g. Straight chain organic materials formed during materials, created at the time of pyrolysis by the catalysis of the NFM nanocomposites are transformed by the fixation reaction into a carbon matrix with a ring structure. These results means that the whole carbon content increases because of the polymers created by the fixation reaction and biomass matrix components without pyrolysis[19, 20]. Therefore, we confirmed that the iodine adsorptivity increases because of the increase in fixed carbon content.

Table 2. Remove rate for 50 µmol/mol of ammonia, hydrogen sulfide and triethylamine gases at 25 °C.

| Gases | Time (hr) | Blank conc. (µmol/mol) | Measure conc. (µmol/mol) | Remove rate (%) |
|------------------|-----------|------------------------|--------------------------|-----------------|
| Ammonia | 0 | 50 | 50 | 0 |
| | 1 | 49 | N.D. | 100 |
| | 2 | 48 | N.D. | 100 |
| Hydrogen sulfide | 0 | 50 | 50 | 0 |
| | 1 | 49 | N.D. | 100 |
| | 2 | 48 | N.D. | 100 |
| Triethyl amine | 0 | 50 | 50 | 0 |
| | 1 | 49 | N.D. | 100 |
| | 2 | 48 | N.D. | 100 |

In order to determine the remove rate of ammonia, hydrogen sulfide and triethylamine, we used a carbonized sample (600 °C / 2 hr) and conducted a remove rate test using the impregnated to NFM 5000 mg/L of

nanocomposites. The 20g of sample was put in to a reaction tank for 0, 1, and 2 hr at 25 °C under a 50 $\mu\text{mol/mol}$ of ammonia, hydrogen sulfide and triethylamine gases, respectively. (See table. 2) From above results, we identified that the sample shows a good removal capabilities for malodorous gases.

Table 3. Remove rate for 50 $\mu\text{mol/mol}$ of benzene, toluene and formaldehyde gases at 25 °C.

| Gases | Time (hr) | Blank conc. ($\mu\text{mol/mol}$) | Measure conc. ($\mu\text{mol/mol}$) | Remove rate (%) |
|--------------|-----------|-------------------------------------|---------------------------------------|-----------------|
| Benzene | 0 | 50 | 50 | 0 |
| | 1 | 49 | N.D. | 100 |
| | 2 | 48 | N.D. | 100 |
| Toluene | 0 | 50 | 50 | 0 |
| | 1 | 49 | N.D. | 100 |
| | 2 | 48 | N.D. | 100 |
| Formaldehyde | 0 | 50 | 50 | 0 |
| | 1 | 49 | N.D. | 100 |
| | 2 | 48 | N.D. | 100 |

Also, we determine the remove rate of VOCs (benzene, toluene and formaldehyde), we used a carbonized sample (600 °C / 2 hr) and conducted a remove rate test using the impregnated to NFM 5000 mg/L of nanocomposites. The 20g of sample was put in to a reaction tank for 0, 1, and 2 hr at 25 °C under a 50 $\mu\text{mol/mol}$ of benzene, toluene and formaldehyde, respectively. (See table. 3) Even in the case of table 3, we got similar results with the shown in Table 2. It was confirmed that the removal ability of a volatile gases.

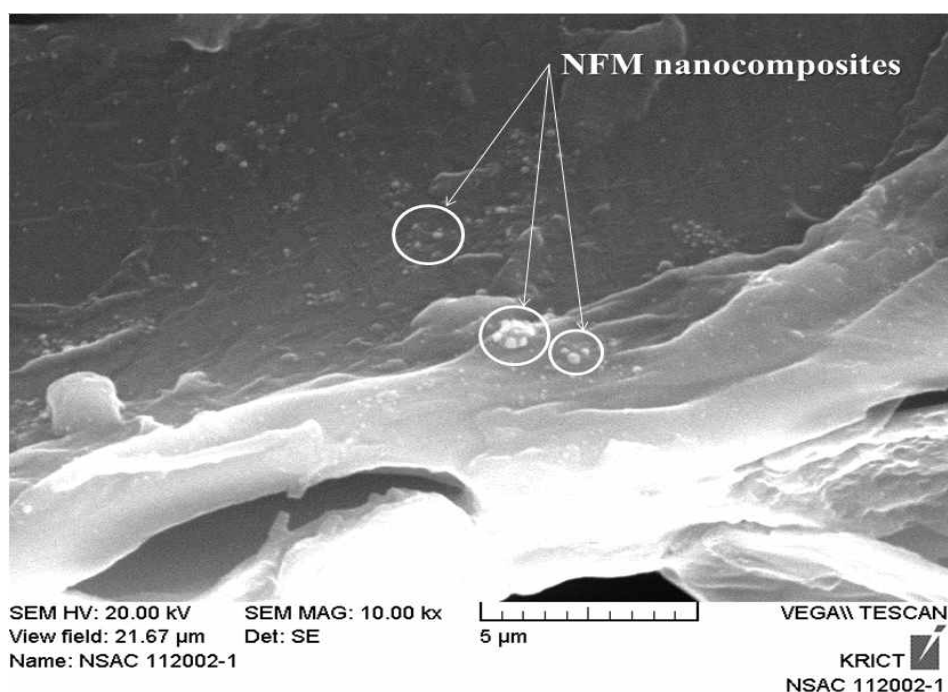


Figure 4. SEM image for 5000mg/L of NFM nanocomposites impregnated carbonized sample.

Figure 4 shows the SEM images of impregnated the 5000 mg/L of NFM nanocomposites. The SEM analysis

showed that the metal was uniformly aggregated on the sample surface. Therefore we confirmed that the NFM-nanocomposites were dispersed into the pores.

4. Conclusions

We impregnated NFM nanocomposites into biomass and determined the optimal conditions for developing highly functional nanocomposites. Because of the NFM nanocomposites, the pyrolytic temperature changed, and SEM revealed changes in the surface state, impregnation state, and pore distribution.

NFM nanocomposites impregnation was found to lead to an increase in the fixed carbon ratio and iodine adsorptivity. Through experiments, the optimal conditions for NFM nanocomposites impregnation were found to be an impregnation time, temperature, and concentration of 2 hr, 40 °C, and 5000 ppm, respectively, and a sample to solution ratio of 1:1.2. For the first heat treatment, the optimal conditions are a treatment time and temperature of 2 hr and 350 °C, respectively, and a 1:1 mixture of air and N₂. For carbonization, the optimal treatment time and temperature are 2 hr and 600 °C, respectively.

For activation, the optimal conditions are a treatment time and temperature of 120 min and 900 °C, respectively, with a CO₂ gas flow rate of 400 cm³/min. We analyzed the physical properties of the functional materials using KS 1082. The iodine adsorptivity for 1000, 3000 and 5000 mg/L of NFM nanocomposites were 368 mg/g, 475 mg/g and 534 mg/g respectively.

Also, the remove rate of malodorous and VOCs were that the sample shows good removal capabilities. Therefore, our sample could be used for the removal of noxious and malodorous gases and for the purification of wastewater.

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