Effect of activation and exfoliation on the formation of carbon nanosheets derived from natural materials

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Abstract. Carbon is abundantly found in nature with a wide range of applications. It can be synthesized through physical and chemical processes. Chemical activation is considered as a very efficient method to obtain carbon with high specific surface area and narrow micropore distribution. Among all the chemical activating agents, alkaline hydroxides such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) are reported to be of high interest in the production of carbon with higher performance. In our research, Nettle stem and peanut shell (natural materials) were used as raw materials for the preparation of carbon. Natural structures of nettle and peanut shell consists of cellulose, which is an important precursor in the preparation of highly ordered carbon nanosheets. Aqueous solutions of KOH and NaOH were used for activation and sulphuric acid (H₂SO₄) was used for exfoliation. The process employed here has yielded a high percentage of carbon nanostructured particles.

1. Introduction

Carbon is commonly found in nature in many forms like diamond, fullerenes, graphite etc and different dimensions like such as activated carbon, graphite, graphene, carbon nanotube, carbon nanosheet, carbon fibre, etc. Applications of activated carbon include abrasives, electronics and water treatment [1-2]. Carbon can be activated either by physical or chemical processes. Chemical activation is found to be an effective method for obtaining carbon with high specific surface area and least micropore distribution [3]. Alkaline hydroxides, especially potassium hydroxide (KOH) and sodium hydroxide (NaOH) are well-known chemical activating agents for activated carbon preparation. These activating agents can be used in tandem with many different carbonaceous precursors and provide flexibility to the process. Hence, understanding the working mechanism of these activating agents in producing chemically activated carbon is essential [4-5]. Liquid exfoliation is a commonly used method in preparation of carbon. The main liquid exfoliation mechanism consists of ion intercalation, ion exchange and sonication assisted exfoliation. The layered crystal is sonicated in a solvent, resulting in exfoliation and nanosheet formation [6].

The preparation of nanostructured materials from waste materials has been studied in many research works in recent years [7-10]. Peanut and nettle are widely distributed in many parts of the world. Both the precursor materials are inexpensive and readily available for synthesis. An in depth study on these materials will surely reveal their benefits in activated carbon synthesis over many of existing methods. The organic composition of peanut shell and nettle shell consists of cellulose, hemicellulose, and
lignocellulose. All these structures are high in bio carbon and can be used for preparation of activated carbon [11-12].

This research work aims to systematically investigate the effect of different alkaline hydroxide activating agents and the effect of exfoliating acid on the activated carbon nanosheets prepared from natural materials. Aqueous KOH and NaOH were used for activation, H$_2$SO$_4$ was used for exfoliation in the experiments. The developed process is simple and yields a high percentage of carbon particles in a nanostructured form. The results obtained in this work could help to better understand the different activation and exfoliation behaviours observed in natural carbon nanosheets.

2. Experimental methods

2.1 Synthesis of carbon nanosheets
Nettle stems and peanut shells were collected from Miskolc, Hungary. The organic composition of materials was investigated via chemical analysis at Mezolabor - Szolgaltaos Kereskedelmi Kft, Hungary. The cleaning process started with washing and drying chopped nettle stems and peanut shells at 80 °C for 24 hours. To remove metallic oxide or organic compounds the samples were cleaned by HCl [0.5 M] for 24 hours then washed with distilled water and dried at 80 °C for 24 hours. The dried samples were heated up to 450 °C and dwelled for 2 hours in a stainless-steel tube furnace under argon atmosphere. The heat-treated samples (biochar) were milled for 1 hour using mortar, then stirred in aqueous KOH (solute) and NaOH (solute) with a weight ratio of biochar sample: KOH and NaOH = 1: 1 for 1 hour and later dried at 80 °C for 24 hours. The mixed samples were carbonized at 800 °C for 2 hours in a stainless-steel tube furnace under argon atmosphere. Finally, the activated samples were exfoliated in 10 vol% of sulphuric acid and stirred for 1 hour and then washed with distilled water several times until neutral pH is reached. They were dried overnight at 80 °C.

2.2 Characterization
The microstructure and morphology of the samples were investigated using scanning electron microscopy (SEM, ZEISS EVO-MA10, HITACHI S4800 and Helios G4 PFIB CXe), the chemical composition was analysed by using energy-dispersive X-ray spectrometry (EDS, EDAX Genesis and Bruker), the specific surface area was examined by using Brunauer-Emmett-Teller method (BET, Micromeritics TriStar 3000).

3. Results and discussion

3.1 Organic and chemical composition of raw materials
The samples of the raw materials are mainly composed of cellulose, lignin and hemicellulose as shown in Table 1. Nettle stems have higher organic (cellulose and hemicellulose) content than peanut shells. Chemical composition, as studied by EDS, is listed in Table 2. We can see the carbon content in nettle stems and peanut shells is very high and this can only be further increased by carbonization, chemical activation and exfoliation (Table 3).

Table 1. The organic composition of raw materials

| Materials    | Cellulose (wt.%) | Hemicellulose (wt.%) | Lignin (wt.%) |
|--------------|------------------|----------------------|---------------|
| Nettle stems | 49.8             | 15.3                 | 11.9          |
| Peanut shells| 42.7             | 8.4                  | 27.2          |
Table 2. Chemical composition of raw materials (EDS results)

| Dried materials | C     | O     | Si | Zn | K    | Ca    | Mg | S    |
|-----------------|-------|-------|----|----|------|-------|----|------|
| Nettle stems    | 50.80 | 36.03 | 2.45 | -  | 6.98 | 3.08  | 0.26| 0.43 |
| Peanut shells    | 61.55 | 37.69 | 0.04 | 0.72 | -    | -     | -  | -    |

3.2 Microstructure and chemical composition

3.2.1 Nettle stems.
The chemical composition (Table 2) shows the presence of carbon, oxygen, silicon, potassium, calcium, magnesium and sulphur in dried nettle stems. Activated samples with KOH and NaOH have increased carbon content to (93.84 and 91.60 wt.%, respectively) with a small amount of oxygen and other contaminants (Table 3). The microstructure of activated carbon nettle stems with KOH and NaOH is quite similar. But the chemical composition of nettle stems carbon nanosheets (NSCNs) after activation with different alkaline hydroxides were slightly different from each other.

a) NSCNs activated with KOH and exfoliated by H$_2$SO$_4$

After the nettle stem carbon nanosheets were obtained from KOH as an activating agent, they are exfoliated using sulphuric acid. The SEM micrograph of NSCNs exfoliated by sulphuric acid (Figure 1 a) shows a smooth surface and clearly reveals the formation of separated carbon nanosheets with thickness ranging from 42 to 71 nm. EDS results show that carbon nanosheets have very high carbon content 88.71 wt.%.  

b) NSCNs activated with NaOH and exfoliated by H$_2$SO$_4$

The microstructure of NSCNs activated by NaOH and exfoliated by sulphuric acid (Figure 1 b) shows small particles and thin sheets with sharp edges. The thickness of these sheets ranges from 55 to 60 nm. EDS results show that carbon nanosheets mainly contain carbon (91.75 wt.%).

Figure 1. SEM micrograph of NSCNs activated with (a) KOH, (b) NaOH and exfoliated by H$_2$SO$_4$

The structure of the carbon nanosheets after activating with two alkaline hydroxides and exfoliating by sulfuric acid are quite similar (Figure 1 a-b). The smooth surface carbon nanosheets with a large area were clearly observed. By comparing the microstructures, it was found that carbon nanosheets are separated and their surface is clean. During activation, KOH or NaOH can penetrate into the pores of the carbonized material resulting in KOH or NaOH residue. This residue later reacts with the exfoliation acid. The activation and exfoliation processes have increased the specific surface area of
the carbon sheets. The major presence of carbon element (Table 3) indicates the high purity of these samples.

| Table 3. Chemical composition of the nettle stems and peanut shells (EDS results) |
|------------------------------------------|-----------------|-----------------|-----------------|
| Samples | Chemical composition (wt.%) | Activation | Exfoliation | C | O | Other |
| Nettle stems | | | | | | |
| KOH | no | 93.84 | 4.78 | 1.38 |
| NaOH | no | 91.60 | 5.20 | 3.20 |
| KOH | H₂SO₄ | 88.71 | 9.38 | 1.91 |
| NaOH | H₂SO₄ | 91.75 | 7.93 | 0.32 |
| Peanut shells | | | | | | |
| KOH | no | 81.71 | 10.93 | 7.31 |
| NaOH | no | 89.91 | 9.65 | 0.44 |
| KOH | H₂SO₄ | 89.37 | 8.97 | 1.66 |
| NaOH | H₂SO₄ | 90.37 | 8.61 | 1.02 |

3.2.2 Peanut shells

The chemical composition shown by EDS consists of carbon, oxygen and other elements in small amount of dried peanut shells (Table 2). Activated samples with KOH and NaOH have increased carbon content up to (81.71 and 89.91 wt.%, respectively) compared with dried peanut shells (Table 3). The chemical composition of peanut shell carbon nanosheets (PSCNs) after activation with alkaline hydroxides and exfoliating by sulfuric acid is slightly different. Besides the high amount of carbon (more than 80 wt.%), only some elements remained in a small amount (Table 3), similar to NSCNs samples.

a) PSCNs activated with KOH and exfoliated by H₂SO₄

The SEM micrograph of PSCNs activated with KOH and exfoliated by sulphuric acid (Figure 2 a) shows thin nanosheets with thickness varying between 45 to 75 nm. EDS results show that carbon nanosheets mainly contain carbon (89.37 wt.%) (Table 3).

b) PSCNs activated with NaOH and exfoliated by H₂SO₄

The microstructure of PSCNs activated with NaOH exfoliated by sulphuric acid shows small particles, hollow and thin sheets with sharp edges and thickness ranging from 10 to 50 nm.

Figure 2. SEM micrograph of PSCNs activated with (a) KOH, (b) NaOH and exfoliated by H₂SO₄
3.3 Surface properties
The surface property changes including the specific surface area, micropores volume, adsorption and desorption, the average pore diameter of samples was investigated using result from a BET nitrogen adsorption gas. The identification of the activated carbon nanosheets according to the alkaline hydroxide and the exfoliating agent is given in Table 4-5.

3.3.1 Surface properties of nettle stems
The specific surface area of NSCNs activated with NaOH after exfoliating by H₂SO₄ is smaller than the specific surface area of NSCNs activated with KOH (Table 4). The micropore volume of the NaOH activated samples is lower than KOH activated samples, but the average adsorption and desorption pore diameter is higher in the case of NaOH activated samples compared with other samples, especially in NaOH activated sample without exfoliation.

Table 4. BET surface properties of the NSCNs

| Activation | Exfoliation | Specific surface area (m²/g) | Micropore volume (cm³/g) | Adsorption average pore diameter (nm) | Desorption average pore diameter (nm) |
|------------|-------------|-----------------------------|--------------------------|--------------------------------------|--------------------------------------|
| Dried nettle stems |  | 0.17 | 0.0001 | 15.11 | 27.78 |
| KOH | no | 623 | 0.25 | 1.90 | 1.95 |
| NaOH | no | 777 | 0.17 | 2.12 | 2.18 |
| KOH | H₂SO₄ | 705 | 0.29 | 1.92 | 1.93 |
| NaOH | H₂SO₄ | 220 | 0.07 | 2.08 | 2.13 |

3.3.2 Surface properties of peanut shells
The specific surface area of PSCNs activated with NaOH before and after exfoliation by H₂SO₄ is lower than PSCNs activated with KOH (Table 5). The micropores volume of the PSCNs activated with NaOH is lower than KOH activated samples. The average adsorption and desorption pore diameter of the activated and exfoliated PSCNs is less than 3 nm. The qualitative property of carbon nanosheets was confirmed by SEM images and BET. The two investigations assure the formation of carbon nanosheets with a higher specific surface area (which can describe the separation ability of carbon layer from this process) and small pore diameter.

Table 5. BET surface properties of the PSCNs

| Activation | Exfoliation | Specific surface area (m²/g) | Micropore volume (cm³/g) | Adsorption average pore diameter by BET (nm) | Desorption average pore diameter by BET (nm) |
|------------|-------------|-----------------------------|--------------------------|--------------------------------------|--------------------------------------|
| Dried peanut shells |  | 0.29 | 0.0001 | 7.70 | 21.39 |
| KOH | no | 986 | 0.38 | 1.90 | 1.91 |
| NaOH | no | 563 | 0.18 | 2.04 | 2.06 |
| KOH | H₂SO₄ | 1,104 | 0.37 | 2.27 | 2.29 |
| NaOH | H₂SO₄ | 395 | 0.11 | 2.11 | 2.13 |

From the BET results, the type of alkaline hydroxide used highly affects the specific surface area of CNs, especially in KOH activated NSCNs and PSCNs. Due to the solubility in water (at 25 ºC) of KOH (121 g/100 ml) is higher than NaOH (100 g/ml), the boiling point of potassium (759 ºC) is lower than sodium (883ºC). Hence, the diffusion of potassium into the carbon layer is easier comparatively.
and results in higher pore diameter and surface area [13]. Another possible explanation can be found from literature [13-14], the radius of K⁺ is larger than Na⁺ (0.138 and 0.102 nm, respectively), so when the potassium moves between layers of carbon resulting in more carbon separation. Effect of exfoliation is also studied in relation to production of carbon nanosheets in this research [15]. The surface area and pore properties of carbon nanosheets are clearly effected as observed from BET analysis.

4. Conclusions
The carbon nanosheets synthesized from nettle stems and peanut shells using KOH or NaOH activation and H₂SO₄ exfoliation have higher specific surface areas, especially peanut shells with 1,104 m²/g. The chemical activation and exfoliation affect the surface property of carbon nanosheets which can be described in terms of quality of porous carbon. The micropore volume of carbon nanosheets activated with KOH is higher than that activated with NaOH. Pore diameters in the exfoliated NSCNs and exfoliated PSCNs were found to be less than 3 nm which belongs to the micropore range. The developed process is simple and yields a high percentage of carbon particles in a nanostructured form (up to 90 %).

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