Preparation and Characterization of Graphite Waste/CeO$_2$ Composites

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Abstract. In this research, the chemical modification of graphite waste with CeO$_2$ was developed and characterized. Graphite waste was pretreated with mechanical to obtain the size 200 mesh (75 $\mu$m), and thermal methods at 110°C oven for 6 hours. Here, we demonstrate final properties of graphite before modification (GBM), activated graphite (GA) and graphite/CeO$_2$ composite with variation of 0.5, 1 and 2 g of CeO$_2$ (G0.5; G1; G2). The effect of CeO$_2$ concentration was observed. The presence of cerium in modified graphite samples (G0.5; G1; G2) were analyzed using SEM-EDX. The results show that the best surface area was found in G2 is 26.82 $m^2/g$. The presence of CeO$_2$ onto graphite surface does not significantly increase the surface area of composites.

Keywords: Adsorption; Cerium; Graphite waste; Modification

1. Introduction

Adsorption is one of the most widely used processes in industry [1]. The adsorption process is widely used for gas separation processes, removal of pollutants in water, purification of solvents, and as catalysts. Activated carbon is known as the most widely used adsorbent because of its large surface area so that the adsorption ability is good [2,3]. High adsorption capacity of activated carbon is usually associated with high surface area, pore volume, and porosity [1,4].

Although commercial activated carbon is widely used, its use is limited due to high costs [1]. The high initial cost and the need for an expensive regeneration system make it less economical as an adsorbent. The actual cost is an important parameter for comparing the adsorbent material. Adsorbents can be considered as inexpensive if it requires less processing and is abundant in nature. Taking into account these criteria, research on the non-conventional alternatives of adsorbents have been widely conducted. Natural materials, industrial waste materials, agricultural waste and biosorbents can be used as cheap adsorbents for many applications.
The graphite waste is very abundant with availability of 1,000 ton per month and having very low price. From our previous research, these graphite waste samples contained the percentage of carbon is about 75 - 83% that can be utilized as adsorbent with modification with lanthanum for removal of dye [5]. The pinned graphite structure makes it applicable as an adsorbent. However, graphite still has low performance as an adsorbent due to its limited surface area. Thus, the recent research has focused on improving sorbent and expanding efficient system for cost-effective for CO₂ capture [1,3]. Therefore, more efficient sorbent for CO₂ capture is very important to be produced.

Cerium oxide has been the subject of thorough investigations, and has attracted much attention especially in the field of catalysts and catalytic supporters [6]. CeO₂ has attracted a lot of attention because of its excellent nature and has been widely applied in recent years. CeO₂ can provide favorable catalytic activity and provide a large area of chemical surface absorption and improve reducibility [7]. By adding CeO₂, the graphite waste contains more Ce³⁺ ions that provide redox-active sites. CeO₂ can provide favorable catalytic activity and provide a large area of chemical surface absorption [8]. Therefore, in this research, we modified the graphite waste using Ce(NO₃)₂·6H₂O with weight variations of 0.5, 1 and 2 g to increase the BET surface area. The effect of Ce(NO₃)₂·6H₂O concentrations on BET surface area of prepared graphite waste/CeO₂ composites were investigated.

2. Materials and Methods

2.1. Materials

Graphite was obtained from waste of ex-electrolysis cathode graphite from Medan (North Sumatra, Indonesia) which was received in powder form (GBM) and was treated by HNO₃ (65%). Cerium oxide was synthesized over graphite via co-precipitation method using Ce(NO₃)₂·6H₂O and NH₃ aqueous solution (25%).

2.2. Pretreated and Preparation of Graphite/CeO₂

Graphite/CeO₂ obtained from waste graphite pulverized into 200 mesh particle size and heated at 110°C for 6 h. The sample was then activated with 1 M HNO₃ solution. The mixture was stirred continuously for 8 hours at 80°C. The sample filtered and washed with distilled water until the pH neutral filtrate (pH ± 7). The obtained solid was heated at 110°C for 24 hours, and then calcined at 500°C for 3 hours. The resulted sample (GA) was then modified using CeO₂. CeO₂ was precipitated from a solution of cerium nitrate. 0.5, 1 and 2 g of cerium nitrate and NH₃ solution were drop-wise into the sample solution for 30 min and stirred slowly with a magnetic stirrer and reached pH at 9. After one hour of mixing, the sample was dried for 12 hours at 110°C, and then it was calcined at 500°C for 5 hours.

2.3. Characterization

The morphology and structure of the samples were investigated by Scanning Electron Microscopy (SEM) analyzer (JSM-6510LA). For elemental analysis Energy Dispersive X-ray analysis (EDX) was performed by JED-2300, JEOL detector. Also, the specific surface areas of the samples were studied in a Quantachrome CHEMBET 3000 unit applying the standard Brunauer, Emmett and Teller (BET) method. The specific surface area (BET) of nanocomposites was characterized by N₂ adsorption and desorption isotherms obtained at -196°C using a Quantachrome ChemBET-3000. To investigate diagnosing surface functional groups, Fourier Transform Infrared Spectroscopy (FTIR) was conducted in the range of 400–4000 cm⁻¹ wave numbers.

3. Results and Discussion

In this study, graphite before modification (GBM), activated graphite (GA) and modified graphite with variation of 0.5, 1 and 2 g of CeO₂ (G0,5; G1; G2) were characterized by FTIR, SEM-EDX and BET test

3.1. Morphology and composition study
SEM micrograph images of (a) GBM, (b) GA, (c) G0.5 (d) G1, and (e) G2 are shown in Fig. 1 (a-e). In general, Fig. 1(a) shows the smoother surface, almost flat and compact, where the porosity is not observed. SEM micrograph image of GA showed fragile surface (see Figure 1(b)). The activation causes the replacement of K⁺, Na⁺ and Ca²⁺ ions originally inside the graphite waste with H⁺ ions. Also, this substitution results in the release of Al, Mg, Fe and other impurities on the lattice of the layered carbon structure. This makes graphite active. The HNO₃ also oxidized the surface of the graphite resulted hydrophilic surface so that the polar molecules (organic compounds) will have better interaction than the nonpolar molecules. SEM micrograph images of all the graphite/CeO₂ composites shows amorphous, fragile and irregular rounded granules (see Figs. 1(c), (d) and (e)). The formed structure has an irregular shape of particles with certain degree of agglomeration.

![SEM micrograph images](image)

**Figure 1.** SEM micrograph images of (a) GNM, (b) GA, (c) G0.5 (d) G1, and (e) G2

The EDX composition of all samples is shown in Table 1. The carbon content of GBM is only 21.29% and other impurities elements in graphite such as sodium, oxygen, aluminum, fluorine, calcium, iron, and
silicon. The high Al impurity content is due to the remaining aluminum from aluminum smelting process since the graphite waste used in this research was electrode for that process. The other impurity elements may be derived from the mineral additives of the graphite-making process. After activation with the acid treatment by HNO₃ 1 M, the carbon content has increased to be 78.85%, then the impurity content becomes reduced (see Table 1). Most of the impurities are soluble in the HNO₃ and washed out after the treatment. Activated graphite was then impregnated with CeO₂, it shows that there is an increase of CeO₂ content from G0.5 to G1 and to G2. This corresponds to the amount of mass of cerium nitrate added at the time of modification of the graphite.

Table 1. EDX composition of graphite and after modification

|       | GBM  | GA   | G 0.5 | G 1   | G 2   |
|-------|------|------|-------|-------|-------|
| C     | 21.29| 78.85| 7.1   | 6.99  | 4.03  |
| N     | -    | -    | 24.26 | 22.09 | 21.62 |
| O     | 19.15| 16.02| 42.18 | 32.07 | 37.38 |
| Ce    | -    | -    | 19.57 | 25.44 | 26.49 |
| Al    | 15.92| 0.92 | -     | -     | -     |
| Si    | 8.27 | 3.41 | -     | -     | -     |
| F     | 18.18| -    | -     | -     | -     |
| Na    | 9.67 | -    | -     | -     | -     |
| Ca    | 3.88 | -    | -     | -     | -     |
| Fe    | 3.64 | -    | -     | -     | -     |

3.2. FTIR Analysis

Figure 2 showed the FTIR spectra of the synthesized G0.5, G1 and G2 composites. The FTIR spectra with a broad band below 600 cm⁻¹ shows the Ce-O stretch mode to confirm the presence of cerium in modified graphite composites [9]. FTIR results show that the Ce-O stretching modes on modified graphite composites at wavenumber 462, 464 and 458 cm⁻¹. While at a wavenumber at 1000 cm⁻¹ indicated the stretching vibration of C-O.

Figure 2. FTIR spectra of G0.5 G1, G2 composites
3.3. Surface area Analysis

Surface area is a key parameter in nanostructured catalyst and has a great influence on catalytic performance. The larger the surface area, the more the reaction site is available and hence higher conversion is obtained. Table 2 shows the result of BET surface area, it can be seen that non-modified graphite (GBM) has surface area 26.35 m²/g, and after activation using HNO₃ the surface area of the GA is 16.63 m²/g. The decrease in the activation process is because HNO₃ treatment extracted most of the metallic impurities which may form pillar structure in between graphitic sheet. After treatment the graphitic sheets collapsed and decrease the surface area of the GA.

After the activation process, the GA sample was chemically modified with Ce(NO₃)₂.2H₂O via precipitation method. The largest BET surface area was observed for G2 composite (26.82 m²/g). This is due to ceria (CeO₂) was attached to the graphite surface and probably intercalates the graphitic layer. From the analysis of pore distribution, it was found that the pores of all samples of the tested materials were distributed in the mesoporous range. Modification surface of graphite waste using Ce(NO₃)₂.2H₂O have changed the structure of graphite waste, it gives more Ce³⁺ ions on surface, thus they provide more redox-active sites for adsorption. On the other hand, we also observed by modified with Ce(NO₃)₂.2H₂O, the BET surface area of composites does not significantly increase.

| Table 2. BET Surface Area of Sorbents |
|---------------------------------------|
|                                  | BET (m²/g) | Pore Volume (cm³/g) | Pore Size (nm) |
|-------------------------------------|------------|---------------------|----------------|
| GBM                                 | 26.35      | 0.09                | 14.05          |
| GA                                  | 16.64      | 0.05                | 11.53          |
| G0.5                                | 20.03      | 0.06                | 11.67          |
| G1                                  | 18.57      | 0.06                | 12.04          |
| G2                                  | 26.82      | 0.08                | 12.25          |

4. Conclusion

The graphite/CeO₂ composites were synthesized and characterized. Further studies should be carried out to examine the performance of this graphite waste/CeO₂ Composites for further commercial application.

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6. References

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