Journal of Metals, Materials and Minerals, Vol. 33, No. 1, pp. 95-100, 2023

Surface modification of activated carbon from sago waste

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Received date:
2 November 2022
Revised date
17 January 2023
Accepted date:
17 January 2023

Keywords:
Activated carbon;
Oxidative modification;
Porosity properties;
Sago waste

Abstract

In this paper, we analyzed the effect of surface modification on the surface properties of the active carbon from sago waste using varied oxidizers, namely H_2O_2, HNO_3, and H_2SO_4. The ordinary active carbon has an initial surface area of 546.6 $m^2 \cdot g^{-1}$, with a phenol and carboxylic functional group. The porosity, functional groups and morphological surface, together with the chemical composition of activated carbon were examined using a nitrogen adsorption-desorption through the Brunauer Emmett Teller (BET) method and the calculation of Barret-Joyner-Hall (BJH), a Fourier-transformed infrared spectroscopy, and a scanning electron microscopy with energy dispersive spectroscopy. The results found that the modified activated carbon significantly increased surface area and total pore volume. Activated carbon modified using H_2SO_4 oxidizers has the highest surface area value of 853.6 $m^2 \cdot g^{-1}$ and a total pore volume value of 0.585 $cm^3 \cdot g^{-1}$. In addition, the surface modification has changed carbon's porosity from micropore to mesopore, altered the surface functional group from phenol to ether. The surface modification has improved its adsorption capacity and potentially further its application. In conclusion, modifying the surface could make the properties closer to the standards for commercial activated carbon.

1. Introduction

Activated carbon is carbonaceous material treated to increase its surface area, porosity [1,2], and oxygenated functional groups [3,4], contributing to the material's wide range of potential uses. The activated carbon would have a better adsorption capacity with the increased surface area and high porosity, which make it applicable as an adsorbent material. Activated carbon is widely used in heavy metal adsorption [5]. Recently it also reported that the porous adsorbents showed attractive removal efficiency of Alizarin Red dye from aqueous solution [6]. The nanoporous carbon also shown a promising application as a high energy gas storage and gasses separation [7]. Moreover, the use of activated carbons as materials for electrochemical double layer capacitors [8] has made them suitable for wide industrial applications.

The advantage of turning waste to value-added products, has triggered studies to explore more renewable and low-cost precursor material for activated carbon production. One of the most promising sources of activated carbon is made from sago waste, expanding its potential use beyond the current application as traditional food production [4,9,10]. The sago waste is full of lignocellulosic fibers, which makes them ideal to use as activated carbon precursors [11]. In the preliminary research, we revealed that the sago waste from Jayapura region in Papua Province, Indonesia, has been used to produce activated carbon. The carbon material was prepared using a $ZnCl_2$ activator reagent, with a surface area of more than 500 $m^2 \cdot g^{-1}$ and a relatively high carbon content at 40%. A surface chemistry study also found that the activated carbon also consists of phenol and carboxylate groups [4,10].

There are two main stages of fabricating activated carbon, carbonization and activation. In the carbonization process, raw precursor material experiences a thermal treatment to increase carbon content and yield a fixed carbonaceous skeleton [12]. Meanwhile, the activation stage means processing the carbon in physical and chemical processes. The physical process utilizes simple thermal activation in the nitrogen atmosphere [13] and microwave radiation [14]. The raw precursor is impregnated in chemical activation with specific chemical activator agents such as H_3PO_4, $ZnCl_2$, NaOH, $KMnO_4$, and KOH [1]. Moreover, combining physical and chemical activation is an alternative approach to enhance the porosity as well as textural features [15].

In adsorption capabilities, the surface area as well as functional groups of activated carbon materials are very significant parameters to be considered. During the activation process, the oxygen, hydrogen, as well as other heteroatoms from raw materials were bonded with carbons and would form various functional groups, such as carboxyl, phenyl, and lactone groups [3]. These surface functional groups have influenced the porous materials of activated carbon and its adsorption properties. Therefore, additional surface chemical modification might be needed to introduce or remove some surface functional groups. Moreover, previous studies have shown that modified activated carbon's adsorption capacity has proven increased considerably [16,17].

DOI: 10.55713/jmmm.v33i1.1616

In other literature, Sultana et al. have reviewed different methods to increase the adsorption capacity of activated carbon, including chemical, biological, and physical modification. The research found that chemical treatment is the most effective method to raise the adsorptive capacity [18]. The oxidative and reductive processes have modified the chemical surface of activated carbon functional groups [19]. The oxidative modification has improved the content of oxygen-containing functional groups, including phenolic hydroxyl, carboxyl, carbonyl, and ester, and it also enhances the polarity and hydrophilicity of the surface. The primary oxidants used in this process are HCl, H_2SO_4, HNO_3, $HClO_3$, and H_2O_2 [18,19]. The reductive modification mainly concentrates on the high-temperature treatment of activated carbon by applying inert gases such as H_2 and N_2. Reduction in the surface might be the result of a change in the activated carbon's surface structure [19].

This study describes how the adsorption properties and functional groups of activated carbon from sago waste changed after surface modification under three oxidants: H_2O_2, HNO_3, and H_2SO_4. After the modification process, the porosity, functional groups, and surface morphology properties were analyzed to comprehend the pore development in the sago waste's activated carbon.

2. Experimental

2.1 Activated carbon fabrication

First, the sago waste was carbonized at a temperature of 400°C for two hours in a furnace to obtain an acceptable carbon bulk. Then we prepared 5 g of carbon from the sago waste to mix with 25 mL of $ZnCl_2$ 20% solution, and we boiled it at a temperature of 85°C for 4 h to improve the activation process and to obtain the remnants with filter papers. Next, the residue was heated at a temperature of 600°C for 3 h and repeatedly washed using warm distilled water (70°C) to a constant pH of 7. The samples were later dried in an oven at a temperature of 110°C for 2 h to get the activated carbon product. Detailed procedures are available in the previous report [10], and the product was donated as total activated carbon.

2.2 Surface modification procedures

The activated carbon product's surface was modified using 30 wt% H_2O_2, 65 wt% HNO_3, and 98 wt% H_2SO_4 solutions, all of which are oxidative chemical agents. They were mixed with a mass ratio between the chemical agent and activated carbon bulk being 1:1. The mixed solution was stirred at a constant rate (130 rpm) for 4 h at 110°C. The resulting slurry was washed using distilled water repeatedly to a pH of 6.8 and dried back at 110°C for 24 h in the oven [9,20]. The oxidizing chemicals (H_2O_2, HNO_3, and H_2SO_4) utilized in the alteration were given their names as the final product.

2.3 Characterizations

The pore characteristics of activated carbons were defined using nitrogen adsorption with Quantachrome Nova 4200e instrument. Specific surface areas as well as pore volumes were characterized and predicted with the Brunauer Emmett Teller (BET) method and Barrett-Joyner-Halenda (BJH) calculation. Furthermore, the Fourier-transform infrared (FTIR) spectroscopy (The PerkinElmer spectrum IR 10.6.1) was employed to define the functional groups of the activated carbon materials, while the scanning electron microscope (Jeol JSM IT 200) with energy dispersive spectroscopy (SEM/EDS) was used to analyze the morphology and the element composition.

3. Results and discussions

3.1 Porosity

Figure 1 shown the adsorption isotherm trend of the unmodified and modified activated carbons with three different oxidative chemical agents that give us information about the porous structure of adsorbent. Based on the IUPAC (International Union of Pure and Applied Chemistry) classification, the unmodified activated carbon exhibit type I isotherm associated with the microporous structure [21]. However, the structure was transformed from microporous to mesoporous after the modification. The type IV isotherms of all three modified activated carbons show clearly discernible hysteresis at elevated pressures.

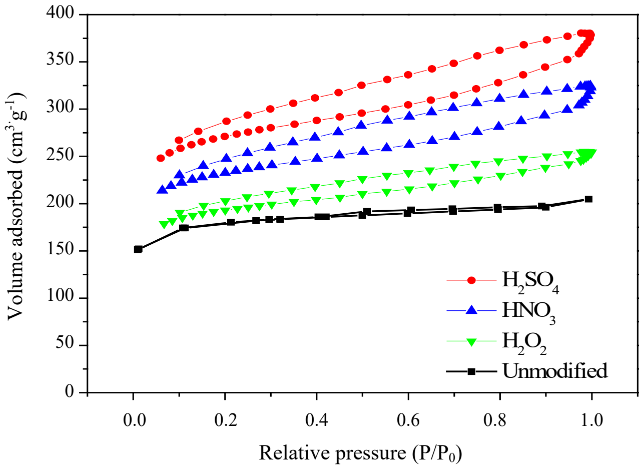

Figure 1. Adsorption-desorption isotherms of the unmodified and modified activated carbons.

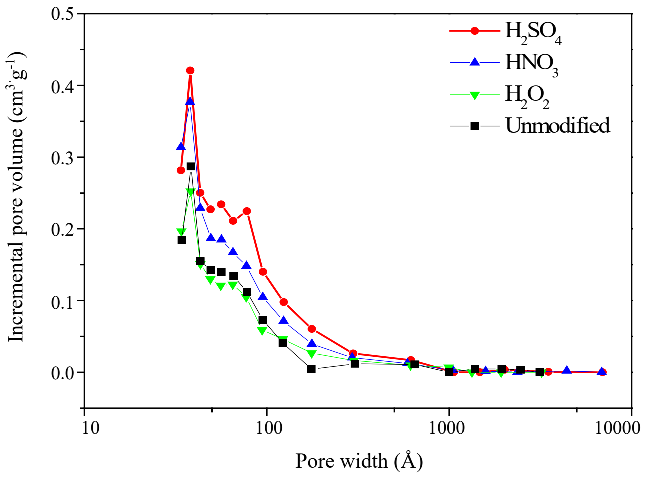

Figure 2. Pore size distribution for unmodified and modified activated carbons.

Table 1. Pore characteristics for unmodified and modified activated carbons.

Oxidative chemical agents	**$V_{Mic.}$ ($cm^3 \cdot g^{-1}$)**	**$V_{Mes.}$ ($cm^3 \cdot g^{-1}$)**	**$V_{Total.}$ ($cm^3 \cdot g^{-1}$)**	**$V_{Mes.}$ / $V_{Mic.}$ (%)**	**Surface area ($m^2 \cdot g^{-1}$)**	**Average pore diameter (nm)**
Unmodified	0.225	0.076	0.301	33.78	546.6	3.32
H_2O_2	0.294	0.101	0.395	34.35	605.2	2.65
HNO_3	0.353	0.146	0.499	41.36	730.8	2.77
H_2SO_4	0.405	0.180	0.585	44.44	853.6	2.78

Table 2. The Fourier-transform infrared peaks identification of the unmodified and modified activated carbons.

Wavenumber (cm^{-1})				**Assignment**
Unmodified	**H_2O_2**	**HNO_3**	**H_2SO_4**	
3,028	3,168	3,171	3,173	ν(O-H) carboxylates group
1,557	1,557	1,568	1,557	ν(C=C) aromatic group
-	1,094	1,069	1,064	ν(C-O) ether group
909	909	-	-	ν(C-O) phenol group
592; 545	666; 605; 562; 555; 534	673; 598; 571; 545	679; 601; 567; 545	ν(C-H) alkanes group

Pore volume, pore size distribution, and surface area are the main parameters affecting activated carbons' adsorption performance [22]. When the reaction between agents and the surface of activated carbon took place in the activation process, the agents touched the surface of carbon and adsorption reaction during the immersing and soaking. From that process, many micropores and creating mesopores. More pores formed resulted in higher surface areas of the product. Therefore, the results obtained in Table 1 clearly show that as the total pore volume increases, it creates the highest surface area.

The porosity characteristic of the final product confirmed that the use of oxidative chemical agents successfully developed new pores, whereas the sulfuric acid H_2SO_4 chemical agents are more favorable to increasing the surface area and the total volume. A review on the influence of chemical modification addressed that an acid treatment induces a positive charge on the surface and then enhances the adsorption of positively charged metal ions [23]. In this study, the sulfuric acid agents tended to enhance the number of pores that lead to more surface area, suggested that sulfuric acid may induce more active site then creating more electrical layer at the surface of carbon, while the other two chemicals possibly acted creating active sites but not as powerful as sulfuric acid did.

3.2 Functional groups

Figure 3 shows the Fourier-transform infrared spectra for sago waste's activated carbon using various activating agents, while Table 2 lists the infrared peaks and their assignments. The modified activated carbon displays alterations, particularly in the fingerprint area, although the region above 1,500 cm^{-1} relatively similar (below 1,500 cm^{-1}). A wide absorption peak detected carboxylate O-H bonds at 3,000 cm^{-1} to 3,200 cm^{-1} in all samples [24].

Additional spectral features shared by all samples included a large absorption band at 1,557 cm^{-1}, whereby a stretching vibration of the C=C aromatic ring structure appeared in all cases [25]. The modified activated carbon exhibits many peaks below 700 cm^{-1} in the infrared spectrum were associated with the out-of-plane bending vibrations in C-H from the alkanes group. The phenolic group may have converted to the ether group during the modification process. The intensity variation indicates a variable extent of substitution [26].

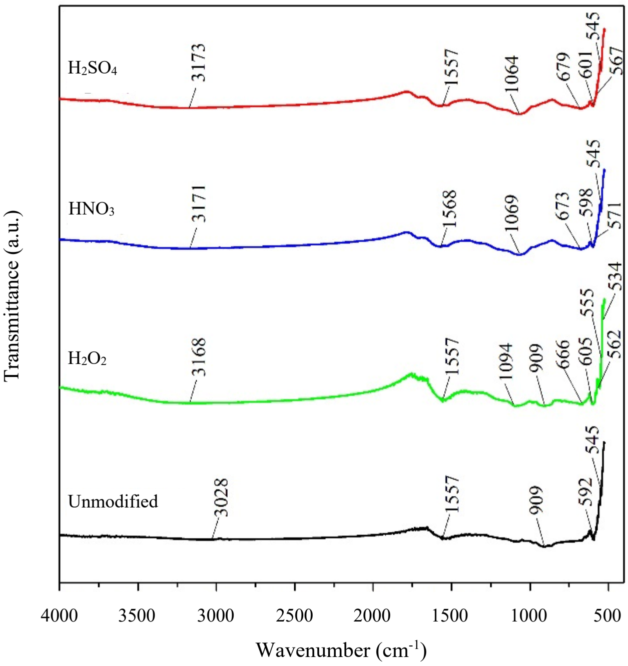

Figure 3. Fourier-transform infrared spectra for unmodified as well as modified activated carbons.

3.3 Surface morphology

Figure 4 displays scanning electron microscopy pictures of the surface morphology at 10k magnification. The morphology images of modified samples confirmed the development of new pores, as analyzed earlier. Furthermore, Figure 4(c) and d show the mesoporous morphological characteristic when the $V_{Mes.}/V_{Mic.}$ value increases to more than 40%. The acquired energy dispersive spectroscopy (EDS) provides elemental composition data for each sample, as summarized in Table 3. The composition of the element in all models was varied. The carbon was increased from unmodified to modified activated carbon, with the highest amount founded from the sample that using H_2SO_4 agent. This process results in a loss of oxygen and shows an increase in surface area. Both lead to changes in the functional group of the modified activated carbon product [24,25].

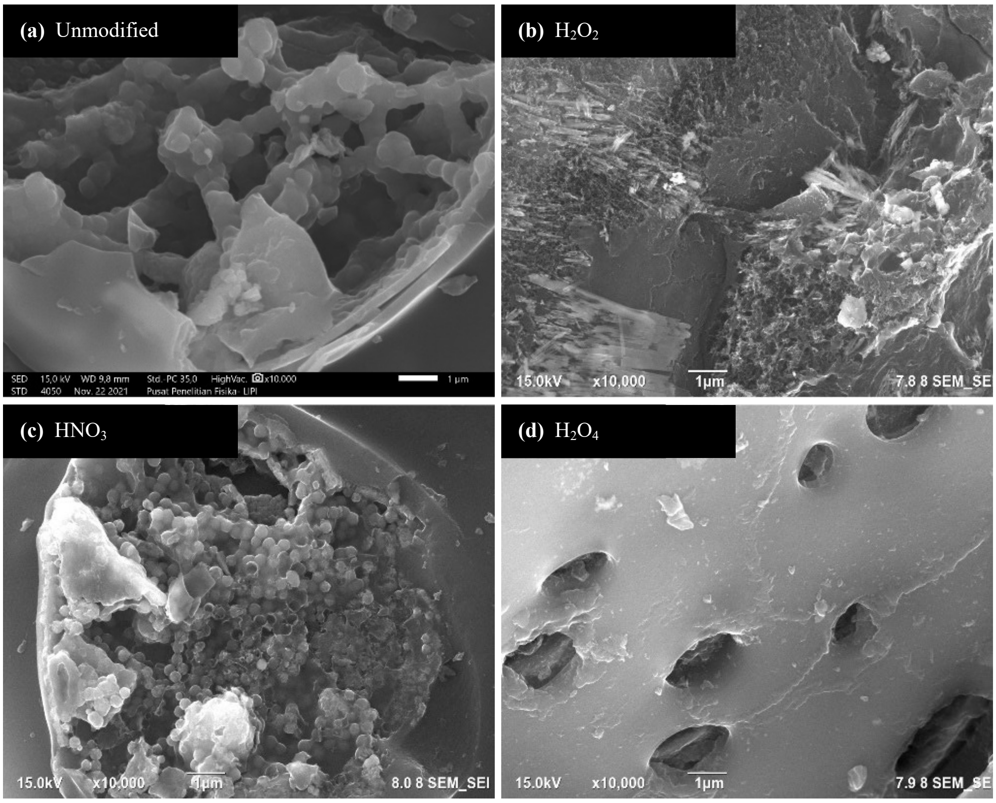

Figure 4. Scanning electron micrographs (10,000×) of the (a) unmodified and (b, c, d) modified activated carbons (Bar length = 1 μm).

Table 3. Elemental composition of the unmodified and modified activated carbons.

Element	**Mass (%)**			
	(a) Unmodified	**(b) H_2O_2**	**(c) HNO_3**	**(d) H_2SO_4**
C	76.5 ± 0.03	79.6 ± 0.01	89.9 ± 0.01	96.2 ± 0.01
O	21.6 ± 0.05	10.5 ± 0.01	-	-
Zn	0.1 ± 0.00	7.0 ± 0.01	5.4 ± 0.01	0.5 ± 0.01
Cl	1.8 ± 0.02	1.3 ± 0.01	4.7 ± 0.01	0.6 ± 0.01
Si	-	0.9 ± 0.01	-	2.6 ± 0.01

The oxidative modification process effectively increases the porosity and adsorption capacity of the sago waste's activated carbon. Commercial grade activated carbon reached a surface value of 500 $m^2 \cdot g^{-1}$ to 1,500 $m^2 \cdot g^{-1}$ [27]. The surface area of this activated carbon is an acceptable method to show its adsorption capacity. Our research shows that there are several applications of the activated carbon which has a surface area in the range of 800 $m^2 \cdot gr^{-1}$, and indicates as an effective adsorbent for both organic and inorganic pollutants [28], and also applicable as a material in supercapacitor electrodes [29]. The activated carbon is also suitable to use as a heterogeneous catalyst, particularly to obtain biodiesel [30]. Therefore, the modified product could be more suitable for commercial activated carbon. Further study on the effect of the impregnation ratio may elevate the pore size since it was an essential parameter in the modification process.

4. Conclusions

This study presented the influence of the oxidative modification process on the activated carbon properties prepared from sago waste. The experiment results suggested that H_2SO_4, a favorable oxidative chemical agent, has developed the highest total pore volume and surface area of 0.585 $cm^3 \cdot g^{-1}$ and 853.6 $m^2 \cdot g^{-1}$. Another result also revealed that the modified activated carbon had changed from microporous to mesoporous behaviour. At the same time, the infrared spectra also show that the phenolic may shift to the ether group after modification. In conclusion, modified activated carbon has become more suitable as a commercial product.

Acknowledgements

This study was entirely financed by the Education, Culture, Research, and Technology Ministry of Indonesia through the 2022 Higher Education Excellent Fundamental Research Grant with Contract Number: 03/UN20.2.1/PG/DRPM/2022. The authors are grateful to the Advanced Characterization Laboratories in Serpong, National Research and Innovation Agency for the facilities, technical and scientific support through E-Layanan Sains (ELSA), as well as Biomaterial Research Laboratory, Universitas Cenderawasih.

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