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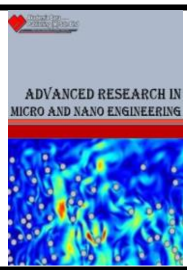

Structural and Optical Properties of Activated Carbon Derived from Eggshell

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ABSTRACT

This research was done to prepare the eggshell as activated carbon (AC) using the simple chemical activation process. Phosphoric acid (H_3PO_4) at different molarities of 0.50, 0.75 and 1.00 M is used as an activation agent. All samples were analysed and characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). SEM images show irregular shapes of carbon. XRD patterns of AC were observed at 29.7°, 36.2°, 40.5°, 43.5°, 47.7° and 48.7° which corresponds to Braggs reflection planes of (201), (105), (107), (207), (206) and (304) respectively. The obtained diffraction peaks show the hexagonal crystal structure of carbon and are well matched with standard JCPDS: 721-616. SEM images show that the structure of AC are fake-like structures and exhibit partial geometrical shape when synthesized at 0.50 M. A broad and strong peak is observed at 1400 cm^{-1} and a sharp peak appears at 872 cm^{-1} due to stretching and bending vibration of the carbonate group present in the samples. The band observed at 1071 cm^{-1} corresponds to the vibration of the phosphate group.

1. Introduction

Activated carbons (AC) are carbon-based compounds with a high interior surface area and porosity [1]. AC-derived products come in a wide range of shapes and sizes, with distinct properties based on the raw material and activation procedure [2]. Because of the manufacture and treatment, activated carbon is a carbonaceous substance that is mostly amorphous in form and has a high porosity [3]. One of two main procedures can be used to form activated carbon: process of physical or chemical activation [2,4].

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Activated carbon has a variety of applications in our daily lives, including advanced wastewater treatment due to its high adsorption ability for organic matter, as well as absorbing and removing indoor pollution and furniture odours [3]. Furthermore, activated carbon has unique properties such as the ability to absorb heavy metal ions and organic contaminants, resulting in a stronger antibacterial action [3]. Chemical catalysts and carriers, gas purification, solvent recovery, and oil decolorization and refining are among the applications for activated carbon [5].

Activated carbon is a non-graphite form of carbon which could be produced from any carbonaceous material [6]. Activated carbon can be formed from many substances containing a high carbon content which are known as carbonaceous substances [7] such as eggshells [2]. Eggshell waste is one of the most emerging abundant waste materials coming from sources such as food [8], poultry hatcheries [9], households [10], homes, fast food industries, restaurants, and food manufacturing industries [11]. The chemical composition of eggshells is made up of 94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate, and about 4% organic matter [2]. Due to the benefits contained in this eggshell, as have been mentioned above, it makes the eggshell suitable for use as the main ingredient in the production of activated carbon.

Due to intrinsic and extrinsic features like high electronic conductivity, high surface area, cheap cost, and affordability to large scale applications, activated carbon-based materials have been used as high-performance supercapacitor applications [5]. This statement has been supported by many researches including carbonized chicken eggshell membrane with 3D architecture was developed by Li *et al.,* as a high-performance electrode material for supercapacitors [12]. Other than that, Jose *et al.,* fabricated highly flexible hierarchical polypyrrole/carbon nanotube on eggshell membranes for supercapacitors and calculated that the areal capacitance of 564.5 mF/cm^2 and volumetric capacitance of 24.8 F/cm^3 respectively [5]. Meng and Deng also built highly flexible hierarchical polypyrrole/carbon nanotube supercapacitors on eggshell membranes and computed that areal and volumetric capacitance of 564.5 mF/cm^2 and 24.8 F/cm^3 respectively [13].

Supercapacitors are a type of energy storage device that sits between batteries and capacitors [14]. Supercapacitors are a bridge between electrochemical batteries, which can store a lot of energy associated with limited power value and dielectric capacitors, which can deliver a lot of power in a short amount of time [15]. Depending on superior cycle stability and high power density [16], supercapacitors (SC) have been given great expectations in the energy storage field [17]. The SC has advantages in applications including a lot of charge/discharge cycles or a longer life is required [16]. Supercapacitors can accept and deliver charge quicker than batteries and can be fully charged and discharged in a matter of seconds [18]. Supercapacitors can provide high specific power (between 0.5 to 5 kW/kg) for a few seconds or longer, resulting in specific energy densities of 0.5 to 10 Wh/kg [15]. There are three different kinds of supercapacitors including metal oxide, carbon/carbon and also electronically conducting polymers [15]. With greater power densities, as well as being more sustainable compared to secondary batteries, supercapacitors have found wide applications in industrial processes, hybride electric vehicles and portable electronics [19]. Bio-derived activated carbon-based materials have been used as high performance supercapacitor applications due to intrinsic and extrinsic properties such as high electronic conductivity, high surface area, low cost, and affordability for large-scale applications [5]. In both acidic and organic electrolytes, it achieved a high energy density supercapacitor of 17.2 and 87.8 Wh/ kg using nitrogen doped commercial activated carbon.

The electric charge is stored in carbon/carbon supercapacitors between a high surface area carbon electrode/electrolyte interface [15]. In this system, when compared to aqueous electrolytes, the usage of organic electrolytes provides for a higher working voltage. A current collector is in contact with activated carbon in the electrode. In the potential window in which the system operates, the current collector must be electrochemically inactive. Activated carbon is the active ingredient in that system. The activated carbon used in supercapacitors must have certain features, including a large specific surface area (m^2/g) to provide a high specific capacitance value, a low resistivity, and a well-adapted microtexture to allow great electrolyte accessibility into the electrode's inner surface.

Large amounts of egg waste are dumped all around the world [20]. The majority of this material is disposed of in landfills without being pretreated [2]. One of the issues cited by landfill managers is that waste eggshells attract vermin because the membrane linked to them emits a bad odour [20]. Activated carbon is expensive [21]. At the moment, intensive research is being conducted to look at low-cost materials being turned into marketable activated carbon alternatives [20]. The high cost of activated carbon, on the other hand, limits its use, driving a surge in research into the development of low-cost replacements to the regularly used activated carbon [2]. Although there are various calcium sources, it is safe to say that eggshells can be used to make activated carbon since they are readily available, eco-friendly, low in cost, and frequently regarded as waste material that is thrown without further use [22]. As a result, making activated carbon from eggshell waste is regarded as one of the most excellent options for turning waste into a valuable product [20].

The aim of this study is to synthesis AC from eggshell using different molarity of activation agent solutions of sodium hydroxide (H_3PO_4). The structural and morphological properties of AC formed using eggshells were investigated and discussed.

2. Methodology

The chicken eggshells waste were washed thoroughly several times with distilled water to remove impurities and all the unnecessary materials adhered to the eggshells. Then, the eggshells were dried in sunlight for a day. Dried eggshells were converted into a fine powder by grinding with mortar until it turned into a fine powder. Then it was kept in a sealed petri dish for further process.

The powdered eggshell was mixed with different molarities (0.50, 0.75 and 1.00 M) of H_3PO_4 solution. The solutions were stirred for 3 hours. The solutions were left overnight (24 hours) at room temperature to let the impregnation agent be absorbed into the eggshell (activation process). The solutions were first washed with distilled water to remove access impregnation agent, filtered and dried (dehydrated) in the oven at 80 ºC for 1 hour. Then, the solutions were carbonized in a furnace at 600 ºC for 5 hours of operating activation temperature and time. Thus, activated carbon was obtained and finally, it was placed in the desiccators to maintain the dryness. Finally, the AC produced was ready to characterize using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy.

3. Results

Figure 1 shows the XRD pattern of synthesized AC using different molarities of H_3PO_4 solution. From XRD pattern shows a mixed crystal phase with a hexagonal structure of carbon. AC samples at 0.50 M of H_3PO_4 solution have an occurrence of a small peak intensity. The peak intensity undergoes an increment when AC samples are produced at 0.75 M solution. However, the peak intensity underwent a decrement again when 1.0 M solution was used. The change in peak intensity is due to the protoporphyrin IX pigment present in the eggshell [23]. The crystalline peaks of AC were observed at 29.7°, 36.2°, 40.5°, 43.5°, 47.7° and 48.7° corresponds to Braggs reflection planes of (2 0 1), (1 0 5), (1 0 7), (2 0 7), (2 0 6) and (3 0 4), respectively. The obtained diffraction peaks show the hexagonal crystal structure of carbon and are well-matched with JCPDS: 721-616 [23]. The remaining peaks belong to $CaCO_3$ [5]. Higher crystalline peaks show the increment of the porosity structure of carbon [23].

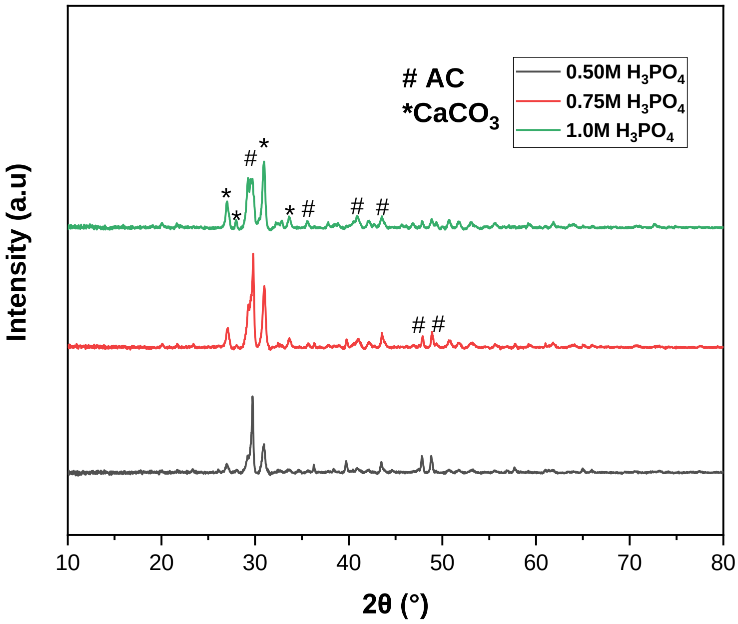

Fig. 1. XRD pattern of at different molarity of H_3PO_4 solution

Functional group and chemical components present in eggshell based activated carbon were recorded using FTIR spectroscopy. Figure 2 shows that at a molarity of 0.50M of H_3PO_4 solution, there is an occurrence of a small peak intensity. The peak intensity undergoes a huge increment at a molarity of 0.75M and decreases again at a molarity of 1.0M. The positions of the bands and peaks can be compared by comparing the vibrational spectra. A broad and strong peak is observed at 1400 cm^{-1} and a sharp peak appears at 872 cm^{-1} due to the stretching and bending vibration of the carbonate group present in the samples. While a band appears around 927 cm−1 with a weak intense band at 715 cm^{-1} which is due to the bending vibration of $CaCO_3$. A weak peak is observed around 1138 cm^{-1} and 1071 cm^{-1} due to the symmetric P–O stretching vibration of the PO_3 2−group which is due to the activating agent used in the materials [5]. The band observed at 1071 cm^{-1} corresponds to the vibration of the phosphate group. P-Carbon is produced when phosphoric acid reacts with phenolic and carbonyl groups of carbon (C-O-P). Microspore growth on the carbon surface is caused by the formation of the C-O-P bond. Nitrogen, oxygen and hydrogen are present and link with other metals on the surface very quickly. The active sites on the activated carbon have increased surface area [23].

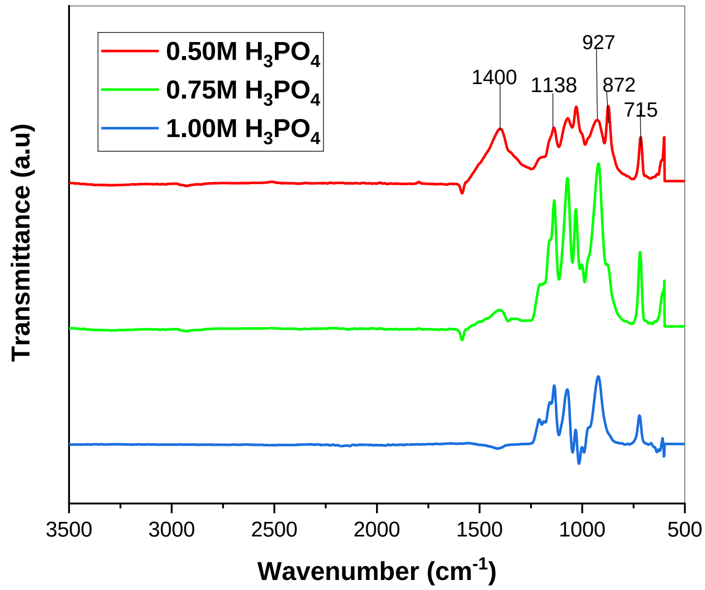

Fig. 2. FTIR spectra of AC at different activation molarity

The structural morphology of AC was visualized by implementing the SEM technique. Figure 3 displays the scanning electron microscope images of AC with a magnification of 5K. It can be seen from the images from Figure 3(b) and (c) that the synthesized particles are highly agglomerated with porous nature which is irregularly distributed over the surface. The porous nature may be attributed to the influence of activating agent H_3PO_4 on the eggshell. The advantage of the porous structure is that it will allow electrolyte penetration which is favourable for ion diffusion, charge transfer and capacitance increases. From Figure 3 (a), the synthesized particles are fake-like structures and exhibit partial geometrical shape. But, the surface morphology is not dense compared to the surface of Figure 3(b) and (c). It could be attributed to the type of eggshells. High porosity causes the charge to increase storage features. Activated carbon that has been created using different biomaterials often has a porous structure. In this study, the AC samples (b) and (c) also show the porous structure of activated carbon [5].

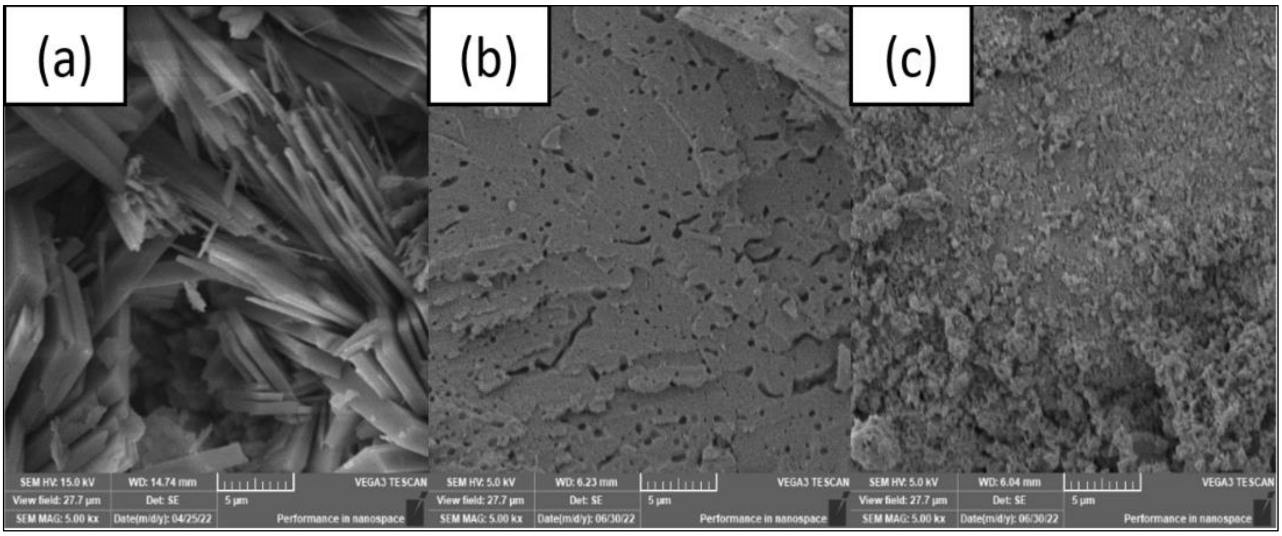

Fig. 3. SEM images of AC samples prepared at (a) 0.50 (b) 0.75 and (c) 1.0M of H_3PO_4 at 5K magnification

The outcome of the energy dispersive X-ray (EDX) analysis detected the elements of carbon, oxygen and calcium which are present in raw eggshell as shown in Figure 4. The analysis (Table 1) confirm the existence of element in chicken eggshell due to its composed by 95-97% calcium carbonate ($CaCO_3$). The presence of phosphorus (P) element also detected in this analysis cause it still remains in samples due to not being properly washed. The existence of this element can be removed by washing with distilled several times to get rid of the contaminants [24].

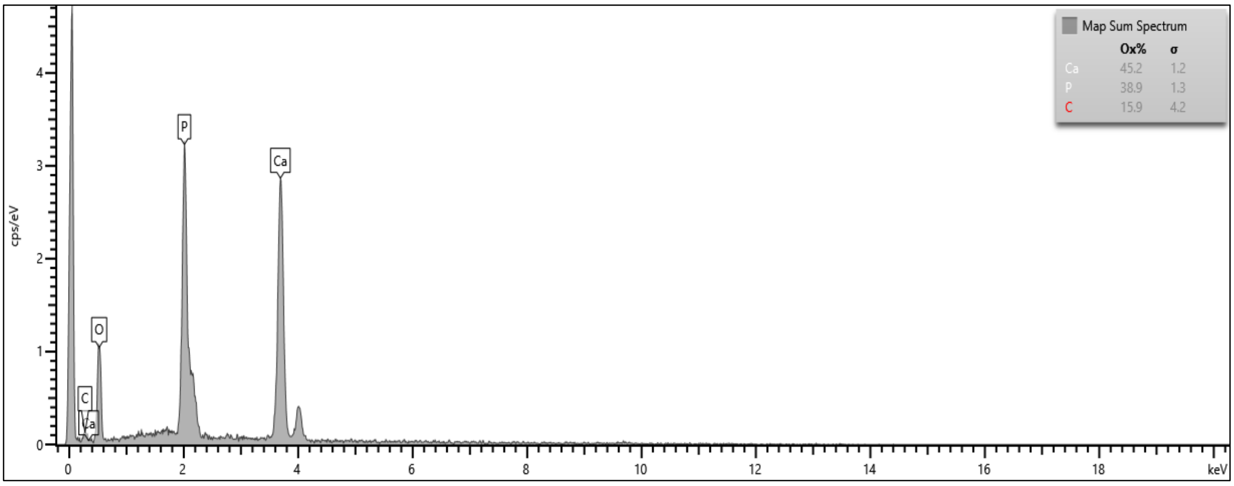

Fig. 4. Electron dispersion spectrum of AC- H_3PO_4

Table 1
Element analysis of AC-H3PO4

Element	Weight (%)	Atomic (%)
C	4.35	7.85
O	46.40	62.83
Ca	32.27	17.45

4. Conclusions

The AC was successfully synthesized using a chemical process using different molarities of H_3PO_4 solution. SEM images show irregular shapes of carbon. AC-H3PO4 showed the particles are highly agglomerated with porous nature which is irregularly distributed over the surface. EDX analysis for AC-H_3PO_4 detected the main elements of carbon, oxygen and calcium. XRD analysis affirmed the formation of AC and the crystallinity coming from affirmed the formation of AC and the hexagonal structure of $CaCO_3$. Functional group and chemical components present in eggshell based activated carbon were recorded using FTIR spectroscopy for both AC-KOH and AC-H_3PO_4. The surface functional groups of AC-KOH are O-H, C-C, C-O and C=O. Meanwhile, AC-H_3PO_4 are P-O and C-O-P. Based on AC-KOH, sample 1:2 is the best sample since SEM analysis shows the highest number of pores produced, XRD analysis shows the highest intensity of a peak and FTIR analysis shows the most increment of peak intensity. Based on AC-H3PO4, sample 0.75 M is the best sample since SEM analysis showed a porous structure with fine pores and cracks, XRD analysis shows the highest intensity of a peak and FTIR analysis shows the most increment of peak intensity. The eggshell waste is selected to form activated carbon since it is readily available, environmentally friendly, low in cost and frequently regarded as a waste material that is thrown without further use. Thus, the results indicate that eggshell waste offers a commercially viable alternative for activated carbon.

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