



# The Effect of Activator Concentration and Urea Doping on the Characteristics of Shrimp Waste Charcoal-Based Activated Carbon as a Supercapacitor Electrode

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**Abstract.** Technological developments cannot be separated from the use of energy to power electronic devices. An electronic device that acts as a store of electric charge (energy) is a capacitor. The capacitor component consists of 2 metal plates separated by a dielectric layer; each plate is given an electrode. To maximize charge storage, the electrode plate is added with materials that have a high specific surface such as activated charcoal (carbon). Activated charcoal can be obtained from the pyrolysis process of materials containing carbon, which is followed by an activation process. This research aims to make activated carbon from shrimp waste which is applied to supercapacitor electrodes. Prior to activation with KOH solution (3, 6, 9 M), the activated carbon was doped with nitrogen in the form of urea with varying mass ratios of charcoal: urea (1:3, 1:5, 1:7). The results showed that the highest capacitance value was obtained at 1:7 urea doping and concentration of activator KOH 9 M, i.e. 25 Farads.

**Keywords:** Shrimp waste · activated carbon · urea doping · supercapacitor · capacitance

## 1 Introduction

The development of increasingly sophisticated technology cannot be separated from the existence of electronic gadgets. These electronic devices require an energy source to operate. Electronic equipment energy is stored in batteries that are lightweight and portable [1]. Energy storage is not only in batteries, but can also be stored in capacitors. The capacitor component consists of two metal plates with electrodes separated by a dielectric layer. Supercapacitors are capable of storing more electric charge than ordinary capacitors. To maximize capacitance, supercapacitor electrodes are usually equipped with materials that have a high specific surface. Activated charcoal (carbon) has a high specific surface, so it is potential to be used as a material for energy storage [2].

Activated charcoal is a carbon material that has many pores which is processed through combustion followed by activation, with a carbon content of 85–95% [3]. The need for activated charcoal as energy storage has increased both domestic and foreign needs. Based on data from the Central Statistics Agency, activated charcoal import has increased by an average of 22% [4]. Indonesia's abundant natural resources, both on land and at sea, make it possible to meet the demand for activated carbon [5]. Charcoal can be used optimally according to its purpose if it has been treated through carbonation and activation processes and adjusted to the desired criteria and quality [6]. The manufacture of activated carbon is influenced by temperature, activator, and activator concentration [5]. The use of activated carbon is very broad, including as a pollutant adsorbent, as well as an electrode material in fuel cells, secondary batteries, and electrochemistry in capacitors [7].

The sources of raw materials for producing activated carbon may come from various vegetable and animal materials which are processed through carbonation and activation, both physical and chemical. Shrimp is a sea-food that is very popular to the public because it tastes delicious and is nutritious for health. Most part of shrimp consumed is meat, while the heads, skins, and tails of the shrimp are simply thrown away as trash [8]. Based on research by [9], shrimp shell contains 40–50% calcium carbonate and 20% chitin which are potential as a carbon producer. Among the uses of activated carbon is as an energy storage electrode material such as in supercapacitors. Supercapacitors are electrochemical double layer capacitors (EDLC), consisting of two electrical double layers separated by a separator [10]. This research aims to study the manufacture of activated carbon from shrimp waste to be applied as a supercapacitor electrode material. To maximize the electric charge storage capacity, prior to activation, carbon is mixed with urea. The effect of doping ratio of nitrogen (urea) to carbon and activator concentration on the characteristics and performance of activated carbon as a supercapacitor electrode was investigated.

## 2 Method

The materials used in the research were shrimp waste, distilled water, toluene, KOH, HCl, dimethyl sulfoxide (DMSO), polyvinylidene fluoride (PVDF), urea, and ethanol. The equipment used includes furnace, magnetic stirrer, copper plate, digital balance, oven, SEM, FTIR, and Cyclic Voltametry (CV) characterization tools.

The shrimp waste was first dried under the sun light for 2 days to remove the water content and facilitate further processing. Before being crushed with a blender, the shrimp waste was dried again in an oven at a temperature of 100 °C until dry. The dry shrimp waste from oven was crushed, and then was sieved with a screen of 100 mesh. The 100 mesh sieved shrimp waste was burned in a furnace at 250 °C for 8 h, until the surface was flat and dark black; it was charcoal. The charcoal obtained was refined again and sieved with a screen of 100 mesh. Before activated using KOH, the charcoal was doped with nitrogen in the form of urea, with mass ratio of 4 g of carbon to 12 g of urea (nitrogen doping ratio 1:3), refluxing at 70 °C followed by stirring with a magnetic stirrer. The mixture was then put into the autoclave reactor for 5 h. After separation using centrifugation, the carbon was washed using distilled water and ethanol. The product

was a carbon sample impregnated with urea. The impregnated carbon was then activated using KOH activator (3, 6, 9 M). The activated carbon was then washed with HCl solution to neutralize KOH. Next, the activated carbon was made to be a composite electrode, added with PVDF and DMSO.

The PVdF acts as an adhesive (matrix) between the aluminum plate and activated carbon, and DMSO as a solvent. The purpose of adding polymer material to activated carbon is as a binder which functions to connect the electrodes to form a compact layer and stick homogeneously in the current collector [11]. PVDF was chosen because it has high mechanical stability, proper swelling properties, and high integration capability on the electrode [12].

The characteristics of activated carbon were measured from the surface morphology of activated carbon and the content of functional groups. The surface morphology of activated carbon was analyzed by Scanning Electron Microscope (SEM), while the functional groups of activated carbon were analyzed by Fourier Transform Infra-Red (FTIR) spectroscopy. The performance of activated carbon as a supercapacitor electrode was measured from capacitance and charge-discharge time. The capacitance was determined by the charge/discharge test method.

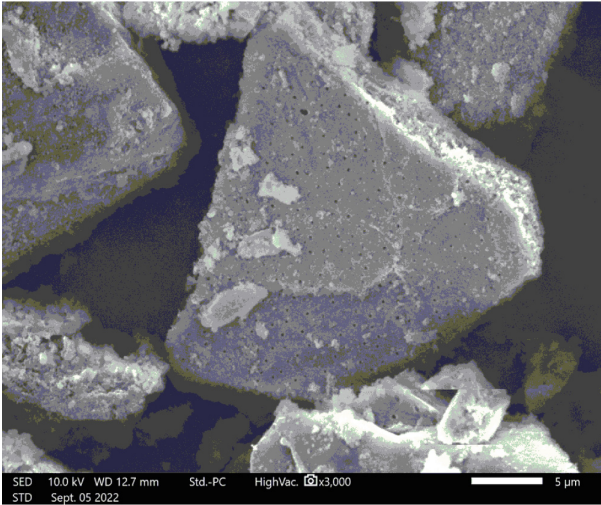
### 3 Results and Discussion

#### 3.1 Surface Morphology of Activated Carbon

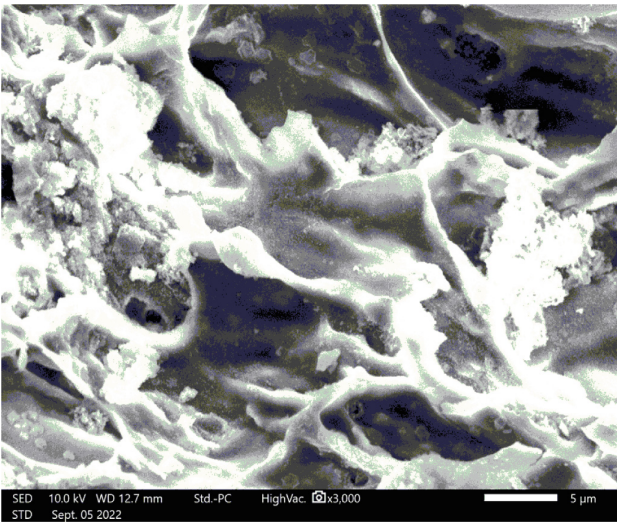
The characterization of activated carbon in the form of surface morphological structures and average pore size using SEM with a magnification of 3000 times is shown in Figs. 1 and 2. The pore size of activated carbon with activator of KOH 9 M at 1:5 urea ratio is smaller compared to 1:7 urea ratio. It can be seen that the more addition of urea, the longer the pores formed and the larger the cavities. 9 M KOH activator with 1:5 urea ratio produced a pore size of 2.52  $\mu\text{m}$  (Fig. 1), while the addition of 1:7 urea ratio resulted in an average pore size of 10.0485  $\mu\text{m}$  (Fig. 2). KOH activator is a strong base that is able to remove hydrocarbon compounds or impurities, which causes changes in the pore structure on the carbon surface, and will affect the electrochemical value [13]. During the activation process the pore structure will experience a shift because the activating agent will push the hydrocarbon residues [3]. The higher the activator concentration, the stronger the solution binds to carbon compounds so that the carbon surface becomes more porous [14]. According to [15] carbonation of biomass using KOH activator results in a more uniform surface morphology and a greater number of pores.

#### 3.2 Surface Functional Groups of Activated Carbon

Analysis of functional groups on activated carbon from shrimp waste was tested using FTIR with an absorption wavelength range of 400–4000  $\text{cm}^{-1}$ . In the sample with activator of KOH 6 M and the ratio of 1:5 urea doping, it shows a change in the peak seen in the C-X bond at a wavelength of 422  $\text{cm}^{-1}$ , and absorption of the C-O group occurs at a wavelength of 1029  $\text{cm}^{-1}$ . The nitrogen group with the N-O bond is seen at a wavelength of 1376  $\text{cm}^{-1}$ . The activated carbon of shrimp waste has absorption



**Fig. 1.** Surface morphology of activated carbon with activator KOH 9 M, ratio of urea doping 1:5.



**Fig. 2.** Surface morphology of activated carbon with activator KOH 9 M, ratio of urea doping 1:7.

patterns of C-O, N-O, C-H, N = O, C = N which indicate that the content of activated carbon-urea-PVDF and keratin. The content of keratin has the potential as a material for making electrodes for energy storage devices [16]. The treatment of activated carbon with the addition of urea as nitrogen doping is traceable to the presence of nitrogen groups in the sample (Fig. 3).

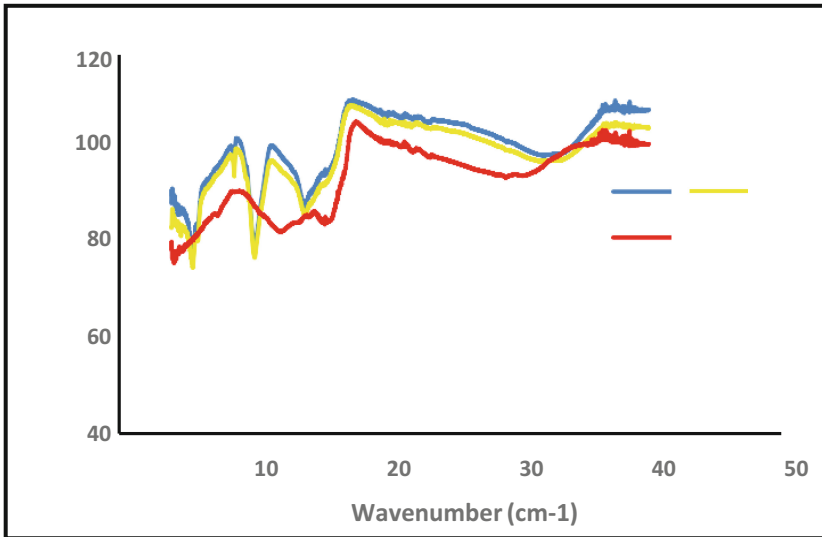


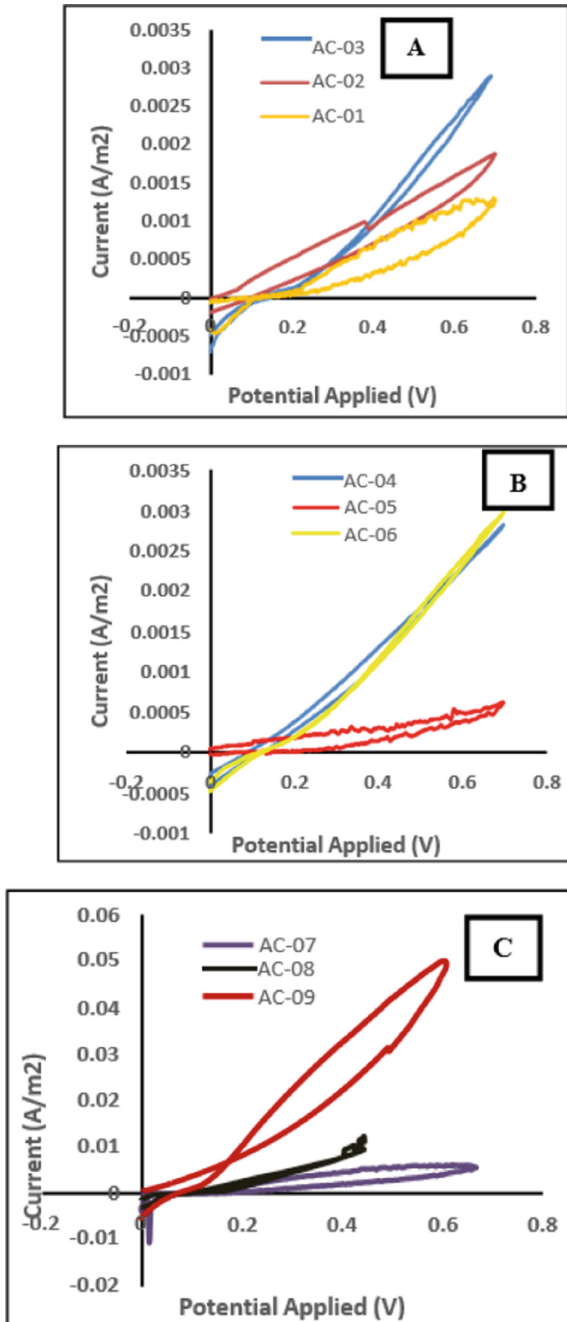
Fig. 3. FTIR spectrum of activated carbon from shrimp waste.

### 3.3 Capacitance

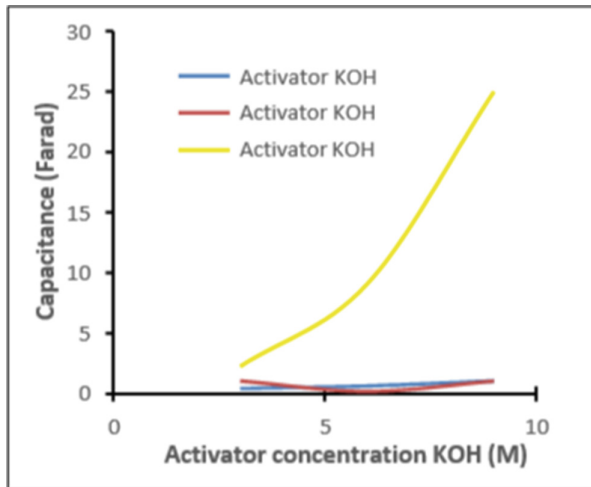
The electrochemical characteristics of the supercapacitor with activated carbon material from shrimp waste with KOH activator and potential applied (v) 0–1 v, at a scan rate of 0.002 V/s is shown in Fig. 4. The shape of the voltammogram curve is affected by charge transfer in the supercapacitor [17]. Figure 4 (A), (B), and (C) are the curves of the relationship between voltage and current at the urea doping ratio of 1:3, 1:5, and 1:7, respectively. It can be seen that the highest voltage and current results were obtained in samples with activator of KOH 9 M. Capacitance values are affected by voltage, current, and scan speed. Research by [18] used a scan speed of 1 mV/s (0.001 V/s) ions, so that electrons diffused longer into the electrode pores. According to [19] the curve is sharp because of the ohmic resistance in the pore. If the charge-discharge current is greater, the current curve will be wider [20].

From the graph of the cyclic voltammogram, the capacitance value is obtained, as shown in Fig. 5. The highest capacitance was obtained in carbon material that had been doped with urea at a ratio of 1:7, and activated with KOH 9 M. Similarly to material from coffee bean biomass, the optimal capacitance was obtained by KOH activator [21]. In bamboo stem material, the higher the concentration of KOH activator increases the capacitance [22, 23].

The maximum capacitance value generated in this study is 25.0033 Farads. This capacitance is relatively low, but still meets the IEC 62391-1:2006 double layer supercapacitor standard, which is 0.6–700 Farads. This relatively low capacitance result is thought to be due to the low carbon surface area, as seen from the morphological structure. In addition, the addition of PVDF matrix as a binder can experience saturation so that it closes the carbon pores. The specific resistance (resistivity) in the PVDF matrix can also affect the material's difficulty in conducting electric current which has



**Fig. 4.** (A) Cyclic voltammogram of KOH activator, doped urea 1: 3 at concentrations of 3.6 and 9 M; (B) KOH activator, 1: 5 urea doped at concentrations of 3.6 and 9 M (C) KOH activator, 1: 7 urea doped at concentrations of 3, 6, and 9 M.



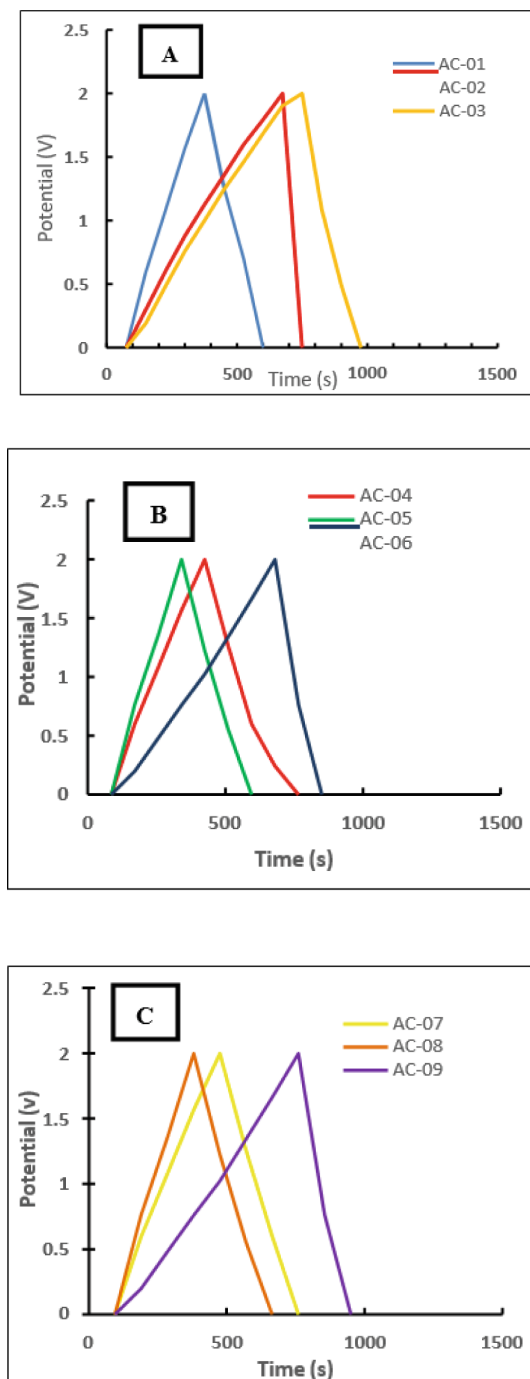
**Fig. 5.** Capacitance value as a function of the urea doping ratio, and KOH activator concentration.

an impact on capacitance [16]. Electrode material from biomass materials produces a higher capacitance as research [24], amounting to 224 F/g.

### 3.4 Charge-Discharge

The performance of supercapacitors besides capacitance is charging and discharging time, where one of the advantages of supercapacitors includes faster charging [25]. Evaluation of the electrochemical properties of the charge-discharge was carried out over a potential range of 0 to 1 V. The data a charge-discharge curve is made which generally has two patterns, namely a peak pattern which indicates charging time, and a transient pattern for discharge time. If the data is entered in one curve, it will form a symmetrical triangle on the voltage variation as a function of time during charging and discharging [26], as shown in Fig. 6.

Figure 6 is a charging and discharging curve at various urea ratios and activator concentrations. The resulting charge forms an imperfect symmetrical triangle and still has an indentation. During the charging process there is an increase in the voltage value, which indicates that the electric field can orient the composite molecules which affect the dielectric polarization. In the discharge process, there is a transfer of electric charge against resistance which can be seen from the graph of the voltage which drops sharply shortly after the discharge process begins. In Fig. 6 (A), (B), (C) the highest voltage reaches 2 V, with varying charging and discharging times. AC-05 was the fastest charging using KOH activator at a concentration of 6 M with a urea doping ratio of 1:5 (Fig. 6 B). The faster the charging and the longer the discharge are, the more efficient the performance of the supercapacitor is.



**Fig. 6.** GCD curve on the ratio of urea, activator, and concentration (A) 1:3 KOH activator 3, 6, 9 M (B) 1:5 KOH activator 3, 6, 9 M (C) 1:7 KOH activator 3, 6, 9 M.



## 4 Conclusion

The concentration of activator KOH and the urea doping ratio affect the morphological structure of the activated carbon surface, where the higher the concentration and urea doping ratio, the more porous the carbon surface is. The FTIR test shows that activated carbon from shrimp waste has oxygen, hydrogen and nitrogen functional groups. At the variable interval studied, the highest capacitance value was obtained with 9 M KOH activator and a 1:7 urea doping ratio, which was 25 Farads. The fastest filling time was obtained from activated carbon activated with 6 M KOH and a 1:5 urea doping ratio, which was 340 s.

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