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Parameter study in preparation of nitrogen-rich-activated carbon for supercapacitors' application using multilevel factorial design

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ABSTRACT

This research aims to study the effect of process parameters on hydrochar modification from biomass on physical and electrochemical properties. Hydrochar is produced by hydrothermal carbonization of biomass at 275 °C for 2 h using an activating agent of CaCl₂. Hydrochar was modified by impregnation at a time variation (1 and 2 h) and doping type (urea, thiourea, and ammonium persulfate). The ratio of hydrochar to doping compound (1:1, 1:2, and 1:3). Activation is carried out by pyrolysis at 800 °C by flowing N₂ and CO₂ gases. The doping ratio and impregnation time significantly increase the yield of activated carbon. The highest value is 39.97 percent for the sample with thiourea and a ratio doping of 1:3 at 2 h (ACT13-2). The main process parameter and the interaction of impregnation time with the doping type affect the surface area of activated carbon. Porosity analysis indicates the product had a mesoporous structure with the largest surface area of 677.44 m² g⁻¹ for the sample with ammonium persulfate and a ratio of 1:1 at 2 h (ACA11-2). The process parameters significantly reduce electrolyte and charge transfer resistance and increase the specific capacitance. The cyclic voltammetry analysis shows the highest capacitance of the supercapacitor cell of 43.25F g⁻¹ was obtained for the sample with urea and a ratio of 1:3 at 2 h (ACU13-2). The endurance test was carried out for 5000 cycles and showed that the supercapacitor cells were stable at 98 percent. Research findings indicate that the hydrochar impregnation method followed by activation can be an effective alternative to produce inexpensive nitrogen-rich activated carbon for supercapacitor applications.

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1. Introduction

Over the past ten years, interest has increased in creating sustainable, green, clean energy storage systems [1]. Because of their extended service life and elevated power density, supercapacitors (SC) are crucial in electrochemical energy storage systems [2]. This includes an energy storage device called an electrochemical capacitor that is more energy–density than traditional dielectric capacitors and more powerful than a battery.

As electric double-layer capacitors (EDLC) electrode materials, porous carbon materials such as activated carbon, carbon nanotubes, and graphene have been the subject of various studies

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[3,4]. Due to its high surface area and low price, activated carbon is chosen over other materials for commercial supercapacitor devices [5]. Conventional activated carbons, on the other hand, have low capacitance and power because of their inappropriate and tortuous pore structure, which limits the accessibility of the electrolyte ions at high charge/discharge rates. Minimizing the ions' time to diffuse via the electrode materials results in excellent power output [6,7].

Pure carbonaceous supercapacitors have low capacitance and energy density, which limits their use. The best method for increasing carbon-based supercapacitor properties is the insertion of heteroatoms, including nitrogen, sulfur, phosphor, and boron [8,9]. Furthermore, heteroatom doping increases electrical conductivity, surface wettability, and electrolyte ion accessibility, adding pseudocapacitance. Expanding the electrode materials' basicity and the electron contributors of the nitrogen atoms during nitro-

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gen (N)-doping makes charge transfer by pseudocapacitance possible. Nitrogen insertion impacts the porosity of carbon-based materials, including the pore size, distribution, and volume, in addition to their surface area and ability to operate as electron donors [10].

Oil palm empty fruits bunch (OPEFB), produced at a 46 million ton per year rate in Indonesia [11], is a plentiful and complimentary sustainable plantation waste of palm oil called lignocellulose. It has historically been utilized as mill boiler fuel, fertilizer after burning, and mulch for palm oil plants. The creation of porous carbon for energy storage using this biomass has been the subject of numerous studies. Due to their low nitrogen concentration, they show a moderate-gravimetric capacitance, which resists their best application at large energy-specific supercapacitors. Due to this reason, it is possible to increase the devices' gravimetric capacitance by mass-producing carbon material from biomass waste with a high nitrogen concentration under varied experimental conditions [12,13].

In the current developments, hydrothermal carbonization (HTC) is gaining weightiness to restore carbonaceous materials due to its ability to produce hydrochar with a more significant oxygenated functional group substance and then use it to create activated carbon with requested characteristics [14]. Hydrothermal reactions in water occur at high temperatures and pressures of 180–347 °C and 4–22 MPa, respectively. The main objective is to use raw materials with high moisture content without pre-drying. Due to its ability to process biomass with high water content, the hydrothermal method seems reliable for preparing carbon material from biomass [15].

The activating agents KOH and ZnCl₂ are recommended for improving the surface area and pore structure while reducing nitrogen content in carbon-based materials [16]. According to studies, biomass waste can be chemically activated to produce porous carbon that can be used as an adsorbent by employing calcium chloride (CaCl₂) instead of KOH and ZnCl₂ [17]. Nevertheless, investigation on creating N-rich porous carbon from OPEFB supported by calcium chloride activator must be improved. The method is inexpensive, simple, easy to do, and ecologically beneficial when performed under hydrothermal carbonization and activation conditions. With urea, ammonium persulfate (APS), and thiourea used as nitrogen sources during the hydrothermal and activation processes, this study sought to produce N-modified activated carbons with linked and geared porous structure and the CaCl₂ doping agents' synergistic effects was carefully examined.

2. Materials and methods

2.1 Material and solution

Raw material (OPEFB) was collected from a palm oil factory in Bogor, Indonesia. Merck supplied the chemical compounds, including calcium chloride (99.9 wt%, Merck), hydrogen chloride (37 vol %, Merck), urea (99.9 wt%, Merck), ammonium persulfate (99.9 wt %, Merck), and thiourea (99.9 wt%, Merck). Sigma-Aldrich provided the ethanol (96 vol%, Merck) and polyvinylidene fluoride (99.9 wt%, Merck). At the same time, Xiamen TOB New Energy in Fujian, China, supplied the cell CR2032 for the supercapacitor case and the hydraulic clipping equipment.

2.2 Synthesis N-modified activated carbon

After being cleaned, dried, and ground into 40 to 80 mesh diameters, the OPEFB biomass was treated using a 1 M HF reagent for two hours to reduce ash content. The deashed biomass was evaporated using an atmospheric oven set at 102 °C overnight. Additionally, deashed feedstock and the liquid phase activator were input to the batch reactor and carbonized hydrothermally for one hour at 275 °C. The gasses substance was evacuated using the plastic container in cold conditions utilizing the release valve. The hydrochar and bio-oil were separated and left to dry for a whole night at 110 °C [12,13].

Doping compounds (urea, APS, and thiourea) were combined with hydrochar in mass ratios of 1, 2, and 3 in demineralized water to modify hydrochar. Using a magnetic stirrer, the mixture was stirred for two hours at 80 °C. The hydrochar-doping combination was evaporated and dried for two hours. Additionally, it was turned on by putting it in a tubular reactor on a ceramic boat, raising the working temperature to 800 °C with a thermal rise of 10 °-C min⁻¹, and adding 50 mL of N₂. After the reactor was turned on, the nitrogen gas flow was substituted with carbon dioxide at 50 mL min⁻¹ for two hours [13]. ACO denotes the pure activated carbon product, and the modified activated carbon product is represented by ACXYY-Z. in which X is the initial letter of the doping type (U for Urea, A for APS, and T for Thiourea). YY is the hydrochar doping ratio, and Z is the impregnation time. The response variables measured for all samples to be statistically analyzed were the yield of activated carbon, the activated carbon's surface area, and the supercapacitor cells' capacitance.

2.3 Physical analysis of material

The morphology and elemental makeup of activated carbon were performed utilizing a scanning electron microscope and energy dispersive spectrometer (SEM-EDS). A Bruker D8 Advanced diffractometer (40 kV, 40 mA) with Cu-K radiation was applied to determine the crystallinity of the sample. N₂ adsorption/desorption of material was examined by using a Quantachrome instruments. The Brunauer-Emmet-Teller (BET) method was exerted to compute the material porosity, and the adsorption quantity at 0.9 relative pressure was utilized to get the total pore volume. Moreover, the Barrett-Joyner-Halenda (BJH) technique was taken to estimate the pore size distributions (PSD). The Fourier Transform-Infrared (FTIR) analysis was applied to assess the qualitative functional groups present in the material. Additionally, employing a hypothetical KBr pellet as an example, a Nicolet 6700 FTIR spectrometer accepted the samples' infrared vibrational mode after an average of 24 sweeps, extending from 4500 to 500 cm^{-1} with the extraordinarily high approach at 5 cm⁻¹ targets [13].

2.4 Electrochemical characterization

Activated carbon and 10% polyvinylidene fluoride (PVdF) were used to create the electrode material. The powders were disseminated in ethanol, the dry substance as much as 0.2 g, then was shaped and compressed at 7–10 MPa to produce an electrode with a specific size. A symmetrical electrode with total mass loading of 2.3 mg mm⁻² was used to manufacture a coin cell-type device (CR2302). A 6 M KOH and a Whatman filter were utilized for the electrolyte and separator, respectively, and a mechanical crimping device was applied to stretch the cell.

Utilize a Gamry Reference 3000 potentiostat with a twoelectrode system, the electrochemical properties of the cell were studied, including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) at a range of 0–1 V, and electrochemical impedance spectroscopy (EIS) [7,9]. Additionally, EIS experiments were conducted at a frequency band of 0.1 MHz to 10 mHz. The life cycle analysis was performed using cyclic charge–discharge measurement. To quantify and correlate the gravimetric capacitance of electrode materials, $C_{\rm sp}$ was counted using Eqs. (1) and (2) [18]. H. Rustamaji, T. Prakoso, H. Devianto et al.

$$C_{cell} = \frac{1}{m\nu(V_c - V_a)} \int_{V_a}^{V_c} I(V) dV \tag{1}$$

$$C_{sp} = 4C_{cell} \tag{2}$$

Where *V* is the scan rate (mV s⁻¹), C_{cell} is the cells specific capacitance (F g⁻¹), m is the weight of two electrodes (g), V_c - V_a is the voltage sweep range (V), and a term I(V) state generated current (A).

2.5. Multilevel factorial design

The mathematical model was developed using the ANOVA tables acquired, and the multilevel factorial design was utilized to evaluate all parameters simultaneously [19]. The best circumstances were established by adjusting the values of several elements. Doping type (A), hydrochar to the doping ratio (B), and impregnation period (C) were the three variables used in this investigation. To examine their effects on response variables, the corresponding levels are shown in Table 1. Eq. (3) was used to compute the yield of AC.

$$Y = \frac{M_{AC}}{M_{biomass}} \times 100\%$$
(3)

 $M_{biomass}$ was the weight of OPEFB supplied into the HTC reactor, and M_{AC} and the importance of AC in grams resulted from the pyrolisis procedure.

3. Results and discussions

Table 2 shows the experimental design, yield value, and SAC porosity characteristics, such as BET surface area (S_{BET}), total pore volume (V_{total}), average pore diameter (d_{av}), and the capacitance value of activated carbon-based-supercapacitor cell (Ccell). Fig. 1a shows a graph of activated carbon yield with a standard deviation line for each experiment. Table 2 informs that the increase in doping ratio and impregnation time increases the output of activated carbon. Meanwhile, the doping types give different activated carbon yields, and thiourea provides the highest results. The influence of these three parameters on yield is presented in Fig. 1a. In addition, Table 2 also shows that the primary process parameters affect the surface area of activated carbon and the capacitance value. The increase in the doping ratio and impregnation time increases the surface area of activated carbon and the capacitance of the supercapacitor cells. The significance of the main effects and the interaction of process parameters on yield, surface area, and capacitance are discussed in detail in the statistical analysis section.

Fig. 1b shows the atomic percent in activated carbon, indicating that the addition of urea, thiourea, and APS doped to hydrochar by the activation process managed to create nitrogen bonding in activated carbon [7,9].

3.1 Morphology and structure characterization

Fig. 2a shows the morphology of OPEFB from SEM analysis that does not yet have pores. Fig. 2b shows that ordinary activated car-

Table 1Parameters and levels for experimental design.

| Parameter | Level | Level | | |
|---|------------------|-----------------|-----------------|--|
| | 1 | 2 | 3 | |
| Impregnation time, A Hydrochar/doping ratio, B Doping type, C | 1 1:1 Urea | 2 1:2 APS | 1:3 Thiourea | |

bon (AC0) has a skeletal structure with numerous cavitations. A series of rough holes above the sample surface is correlated to the breakage of lignocellulosic substance at elevated temperatures; consequently, volatile compounds evaporate, leaving newly formed pores [17]. As the temperature rises, the pores on the activated carbon surface are increasingly formed and tidy. An activator that decomposes the carbon structure throughout the carbonization and pyrolysis procedures causes this opening. The discrepancies in the carbon structure loaded with substances broken down throughout hydrothermal carbonization were issued during CO2 activation, consequently establishing the activated carbon pores [21]. Once the activator is removed from the carbon matrix using an HCl solution, porous structures are formed. ACO sample has a clear pore with a partially closed surface.

Meanwhile, Fig. 2c-e shows the morphology of ACU13-2, ACT13-2, and ACA13-2, respectively. The addition of nitrogen doping with an immersion time of two hours generally has a deforming effect that will increase the porosity of the activated carbon material. However, excess addition causes the collapse of the pore structure [10], as shown in Fig. 2c-e. The morphology (i.e., the existence of voids) is critical in addressing energy storage, and cavities can assist in storing electrolyte ions [20]. SEM-EDS study was carried out to determine the atom in the material product, with the outcomes depicted in Fig. 1b. FESEM was conducted to confirm the morphology of modified activated carbon in high resolution. Fig. 2f-h exhibits the porous nature of carbon samples ACU13-2, ACT13-2, and ACA13-2, respectively. The figure shows a thin carbon sheet morphology that is pleated and creased. The ACT13-2 sample shows a higher degree of collapse of the pore structure than the others, which may indicate a smaller surface area [22].

X-Ray Diffraction (XRD) analysis was carried out to see the crystallinity of the modified activated carbon sample. Fig. 3a shows the XRD results of modified activated carbon samples for each type and the variation of doping ratio. The XRD curves of all samples show a broad peak (002) and a weak band (100) at 2θ at about 26° and about 43°, respectively. The vast peak (002) reveals the characteristic non-crystalline carbon, which usually results from the pyrolvsis process, and the existence of the peak (100) implies the presence of graphite carbon in the sample [23]. Meanwhile, Fig. 3b shows the FTIR spectrum for pristine and modified activated carbon with various doping types. There is a peak difference in the 1463 cm⁻¹ band, which is not found in ordinary activated carbon but appears in modified activated carbon. This peak indicates that the nitrogen is successfully bound to the doped carbon with the doping compound. The modified activated carbon use APS doping showed intensity in the bands around 731 cm⁻¹ and 596 cm⁻¹, respectively, showing C = S and S-S bonds [20].

Fig. 4 shows isotherm curves for pure activated and modified activated carbon with various doping types. All samples exhibited a type-IV isotherm (by IUPAC definition) with a clear hysteresis loop in the range $0.10-0.99P/P_0$ and indicated the presence of a mesoporous structure [8]. Furthermore, a slight rise in adsorption in the high-pressure region (P/P₀ > 0.9) indicates macropores' existence. Fig. 4a demonstrates that the adsorption volume varies with various doping, with urea doping giving the highest adsorption, indicating a more mesoporous structure [4]. The mesoporous structure of the sample is further confirmed by the pore size distribution plot in Fig. 4b, which shows the pore diameter of activated carbon in the wide range of 2.5–35 nm. The four samples in Fig. 4b had a pore size distribution with different narrow peaks at about 3.5–5 nm, which verified the effect of adding doping type to the pore structure.

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Table 2

Experimental design activated carbon, yield value, porosity properties, and capacitance of activated carbon-based supercapacitor cells.

| No | Material | Yield (%) | $S_{BET} (m^2 g^{-1})$ | d _{av} (nm) | $V_{total} (cm g^{-1})$ | $C_{cell} (F g^{-1})$ |
|----|----------|-----------|------------------------|----------------------|-------------------------|-----------------------|
| 0 | AC0 | 23.50 | 363.88 | 1.79 | 0.22 | 25.70 |
| 1 | ACU11-1 | 25.29 | 320.51 | 3.36 | 0.27 | 22.96 |
| 2 | ACT11-1 | 25.61 | 234.56 | 3.10 | 0.18 | 21.93 |
| 3 | ACA11-1 | 23.74 | 344.26 | 3.41 | 0.29 | 20.72 |
| 4 | ACU12-1 | 31.39 | 285.41 | 3.11 | 0.20 | 32.08 |
| 5 | ACT12-1 | 32.36 | 202.47 | 3.09 | 0.15 | 29.01 |
| 6 | ACA12-1 | 29.86 | 300.66 | 3.80 | 0.29 | 22.11 |
| 7 | ACU13-1 | 37.55 | 205.24 | 6.53 | 0.17 | 35.01 |
| 8 | ACT13-1 | 36.11 | 151.57 | 1.72 | 0.06 | 33.59 |
| 9 | ACA13-1 | 36.57 | 288.57 | 3.86 | 0.18 | 28.25 |
| 10 | ACU11-2 | 25.03 | 640.61 | 3.09 | 0.73 | 31.90 |
| 11 | ACT11-2 | 25.42 | 334.27 | 3.81 | 0.20 | 33.82 |
| 12 | ACA11-2 | 27.71 | 677.55 | 3.10 | 0.31 | 22.61 |
| 13 | ACU12-2 | 32.21 | 477.51 | 5.80 | 0.43 | 34.88 |
| 14 | ACT12-2 | 33.05 | 279.20 | 2.04 | 0.15 | 21.43 |
| 15 | ACA12-2 | 33.39 | 558.76 | 2.91 | 0.32 | 31.05 |
| 16 | ACU13-2 | 38.75 | 445.18 | 3.80 | 0.30 | 43.22 |
| 17 | ACT13-2 | 39.97 | 236.16 | 3.10 | 0.07 | 26.38 |
| 18 | ACA13-2 | 38.53 | 440.24 | 8.90 | 0.30 | 34.99 |



Fig. 1. (a) The effect of doping ratio to yield of N-rich activated carbon at various types of doping and (b) percent of elements in activated carbon samples measured by SEM-EDS.

3.2. Electrochemical characterization

The electrochemical characteristic of all supercapacitor cells was evaluated using a Potentiostat/Galvanostat/ZRA. The CV measurement examines supercapacitors' capacitance. Fig. 5a depicts the CV curve for carbon-based supercapacitors at a scan rate of 2 mV s⁻¹. Four samples' curves had an oblique parallelogram form without redox peaks, implying a quick charge–discharge activity by small total resistance and elevated electrical delivery capacity. The ACU13-2 curve presented the highest covered region amongst the materials, denoting the most significant capacitance.

The GCD curves for ordinary and modified activated carbon at 50 mA (0.2 A g^{-1}) are presented in Fig. 5b. The resulting curve has a triangular symmetrical form with a poor voltage (IR) drop, typical of carbon-made supercapacitor devices. Meanwhile, the IR drop exhibits unperfect charge/discharge performance.

Fig. 5c depicts the Nyquist plot from EIS analysis, consisting of three regions: semicircle, slant (45 \circ), and vertical (90 \circ) curve. In addition, the resistance (R_s) of the electrolyte is defined at the start of the semicircle. The medium–high-frequency curve indicated semi-circular loops, implying that charge transfer resistance (R_{ct})

influenced the cell's impedance. The curve's sloped section contributes to the ion diffusion resistance into the electrode pore (R_w) [24]. The imaginary area of the impedance raises at a lower frequency, correlating to carbon's ideal capacitive behavior. The resistance values for the four supercapacitor cells calculated from a single semi-circular range along the x-axis from high to low frequencies are listed in Table 3. Fig. 5c and Table 3 show that R_s of ACU13-2 < ACAT3-2 < ACA13-2 < ACO and the smallest R_{ct} are on ACU13-2 < ACA13-2 < ACT13-2 < ACO. While the R_w values for the four samples did not differ significantly, which could be due to the relatively similar distribution of the pore size of the material to that of the mesoporous structure. This research finding shows that modifying activated carbon by applying nitrogen dopant can decrease R_s and R_{ct} , following the results of other studies [7].

A cyclic charge–discharge (CCD) test was applied to validate the cell's cyclic consistency and resilience, as shown in Fig. 5d. During a prespecified cycle, potential and current were applied to gain the cell's charge–discharge. The coulombic efficiency (CE) and capacitance retention (CR) parameters were also utilized to calculate the cell's durability. The CE reflects the current ratio of discharge



Fig. 2. SEM images of (a) OPEFB, (b) AC0, (c) ACU13-2, (d) ACT13-2, (e) ACA13-2, FESEM image of (f) ACU13-2, (g) ACT13-2, and (h) ACA13-2.

to charge time in the constant current [25], whereas the CR is the capacitance proportion of the present to the first cycle. Fig. 5d shows the value of capacitance retention (CR) and coulombic efficiency (CE) for ACU13-2-based supercapacitor cells, which indicates that urea-doped activated carbon is relatively stable at 5000 cycles. An elevated CE value indicates a poor danger of undesirable reactions at the electrode surface [12].

3.3 Multilevel factorial design analysis

3.3.1. Effect of the parameters on activated carbon yield

The effect of experimental variables on activated carbon yield was analyzed using a multilevel factorial system that included statistical parameters and plot effects. The modified activated carbon yield stated in percent by weight was afterward analyzed

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Fig. 3. (a) The XRD analysis and (b) FTIR analysis of some of the samples of pristine and modified activated carbon.



Fig. 4. (a) N₂ isotherm adsorption-desorption curve and (b) pore size distribution.

by analysis of variance (ANOVA), which was used to determine the interaction among the primary factor relations. The primary effect on the yield value depends on the P-value with a conviction extent of > 95% [27] [26,27]. The yield values generated from 18 runs are within reach of 23.74 and 39.97%, and as a response variable to factors and levels, are stated by the equation below:

$$\begin{split} Y_1 &= 31.836 - 0.894A_1 + 0.894A_2 - 6.369B_1 + 0.292B_2 \\ &+ 6.077B_3 - 0.133C_1 + 0.251C_2 - 0.118C_3 + 0.307A_1B_1 \\ &- 0.031A_1B_2 - 0.276A_1B_3 - 0.307A_2B_1 + 0.031A_2B_2 \\ &+ 0.276A_2B_3 + 0.601A_1C_1 + 0.167A_1C_2 - 0.768A_1C_3 \\ &- 0.601A_2C_1 - 0.167A_2C_2 + 0.768A_2C_3 - 0.174B_1C_1 \\ &- 0.202B_1C_2 + 0.376B_1C_3 - 0.196B_2C_1 + 0.326B_2C_2 \\ &- 0.131B_2C_3 + 0.369B_3C_1 - 0.124B_3C_2 - 0.246B_3C_3 \end{split}$$

 Y_1 is the response or yield of modified activated carbon; *A* is the impregnation time (1 and 2 h); *B* is the doping/hydrochar ratio (1, 2, and 3); and *C* is the type of doping compound (urea, thiourea, and APS). The correlation coefficient (\mathbb{R}^2) value in Eq. (5) is 98.98%, and there is a good relationship between the variables with a good response. The interaction effect is also easy to calculate and

test using ANOVA, and the analysis output is shown in Table 4. Based on the statistical parameters, variables A and B have P values less than 0.05, indicating that the activated carbon yield model significantly responds to changes in time and doping ratio.

A Pareto diagram is used to determine how big and how significant the effect of experimental variables is on the modified activated carbon yield. This quantity can show the direct value of the expected impact from the most effective to the smallest. The significance value determines the line graph for truthful significance. A Pareto chart of the standard effect on the yield of modified activated carbon can be seen in Fig. 6a, where the bar chart lines representing factors *B* and *A* intersect the reference line at 2.78. This value means that the doping ratio and impregnation time significantly affect the yield model at the 0.05 level.

The plot of the main effects and interactions can be seen in Fig. 6b, which shows the impact of variables on yield. Fig. 6b shows an impregnation time of 2 h and a doping ratio of 3, which can be associated with the highest modified activated carbon yield. Fig. 6c shows that the doping type influences the relationship between impregnation time and yield but not the doping ratio. The kind of doping influences the relationship between doping ratio and surface area.

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Fig. 5. (a) CV curve, (b) GCD curve, (c) EIS Nyquist plot, and (d) cyclic stability of ACU13-2 based-supercapacitor.

Table 3The resistance value of activated carbon-based supercapacitor.

| No. | Material | $R_{\rm s}\left(\Omega\right)$ | $R_{\rm ct}\left(\Omega\right)$ | $R_{\rm w}\left(\Omega\right)$ |
|-----|----------|--------------------------------|---------------------------------|--------------------------------|
| 1 | AC0 | 2.45 | 3.05 | 0.41 |
| 2 | ACU13-2 | 0.41 | 0.74 | 0.45 |
| 3 | ACT13-2 | 1.15 | 2.36 | 0.42 |
| 4 | ACA13-2 | 1.31 | 1.13 | 0.43 |

The longer the impregnation time, the more intense the interaction between the doping compounds with hydrochar, and the more significant and robust the bond formation opportunities [27]. The activation process was conducted at 800 °C with a thermal rate of 10 °C min⁻¹ and atmospheric pressure. During the activation process, the thermal decomposition of doping precursors (urea, thiourea, and APS) produces NH₃ and cyanic acid (HOCN). As the temperature rises, some polymerized compounds such as biuret, ammelide, and cyanuric acid are formed at about 150 ~ 350 °C

| Table 4 | | | |
|----------|-------------|--------|--------|
| ANOVA fo | r activated | carbon | yield. |

and decompose at higher temperatures (>360 $^{\circ}$ C). Since the reaction temperature is above 600 $^{\circ}$ C, the leading gases that react are NH₃ and HOCN [28].

3.3.2. Effect of the parameters on capacitance

The average capacitance resulting from 18 experiments is in the range of 20.72 and 43.22F g⁻¹. The factorial regression of the response variable (capacitance) to the experimental factor and level is expressed by Eq. (7).

$$Y_{2} = 29.219 - 2.246A_{1} + 2.246A_{2} - 5.627B_{1} + 0.033B_{2} + 5.594B_{3} + 4.123C_{1} - 1.526C_{2} - 2.597C_{3} + 0.357A_{1}B_{1} - 0.149A_{1}B_{2} - 0.208 A_{1}B_{3} - 0.357A_{2}B_{1} + 0.149A_{2}B_{2} + 0.208A_{2}B_{3} - 1.079A_{1}C_{1} + 1.762A_{1}C_{2} - 0.683A_{1}C_{3} + 1.079A_{2}C_{1} - 1.762A_{2}C_{2} + 0.683A_{2}C_{3} - 0.28B_{1}C_{1} - 0.39B_{1}C_{2} + 0.67B_{1}C_{3} + 0.11B_{2}C_{1} - 0.03B_{2}C_{2} - 0.07B_{2}C_{3} + 0.18B_{3}C_{1} + 0.42B_{3}C_{2} - 0.60B_{3}C_{3}$$
(5)

| Source | Degree of freedom | Sum of square | Mean of square | F-value | P-value |
|----------------------|-------------------|---------------|----------------|---------|---------|
| | | | | | |
| Model | 13 | 488.546 | 37.580 | 27.45 | 0.003 |
| Linear | 5 | 480.475 | 96.095 | 70.18 | 0.001 |
| Α | 1 | 14.383 | 14.383 | 10.50 | 0.032 |
| В | 2 | 465.527 | 232.764 | 169.99 | 0.000 |
| С | 2 | 0.566 | 0.283 | 0.21 | 0.822 |
| Variable interaction | 8 | 8.071 | 1.009 | 0.74 | 0.670 |
| A•B | 2 | 1.030 | 0.515 | 0.38 | 0.709 |
| A•C | 2 | 5.869 | 2.934 | 2.14 | 0.233 |
| B•C | 4 | 1.173 | 0.293 | 0.21 | 0.918 |
| Error | 4 | 5.477 | 1.369 | | |
| Total | 17 | 494.023 | | | |



Fig. 6. (a) Pareto graph of standardized effect with yield as a response at = 0.05, (b) main effect, and (b) interaction effect parameter on modified activated carbon yield.

 Table 5

 ANOVA capacitance of modified activated carbon-based supercapacitor cells.

| Source | Degree of freedom | Sum of square | Mean of square | F-value | P-value |
|----------------------|-------------------|------------------|-------------------|---------|---------|
| Model | 13 | 657.070 | 50.544 | 7.99 | 0.029 |
| Linear | 5 | 624.974 | 124,995 | 19.75 | 0.006 |
| Α | 1 | 90.765 | 90.765 | 14.34 | 0.019 |
| В | 2 | 377.787 | 188.894 | 29.85 | 0.004 |
| С | 2 | 156.421 | 78.,211 | 12.36 | 0.019 |
| Variable interaction | 8 | 32.097 | 4.012 | 0.63 | 0.730 |
| A•B | 2 | 1.159 | 0.579 | 0.09 | 0.914 |
| A•C | 2 | 28.421 | 14.210 | 2,25 | 0.222 |
| B•C | 4 | 2.517 | 0.629 | 0.10 | 0.977 |
| Error | 4 | 25.310 | 6.328 | | |
| Total | 17 | 682.381 | | | |

The correlation coefficient (R^2) of equation (7) is 96.29%, indicating that the equation stating the response to the experimental variable is relatively good.

The effect of the interaction of experimental variables on capacitance was calculated and tested using ANOVA, and the parameter values are presented in Table 5. According to statistical parameters in Table 5, variables *A*, *B*, and *C* have P values less than 0.05. This shows that the modified activated carbon-based supercapacitor cell capacitance model significantly responds to changes in impregnation time, doping ratio, and doping type.

The Pareto chart Fig. 7a shows a bar chart representing factors *B*, *A*, and *C* intersecting the reference line at 2.776. This indicates that the doping ratio, impregnation time, and doping type are sta-

tistically significant at 0.05 in the modified activated carbon-based supercapacitor model.

Fig. 7b shows the effect of a single parameter where the three intersect the horizontal dotted line in the middle of the curve, indicating that the three parameters significantly affect capacitance. The main effect plot in Fig. 7b shows that an impregnation time of 2 h, a doping ratio of 3, and the type of urea doping can be associated with the highest capacitance.

Meanwhile, Fig. 7c shows the interaction effect of the parameters where the parallel lines indicate the interaction effect between the parameter, which is not significant on capacitance. On the other hand, the intersection line between the parameters suggests that the interaction effect between the parameters is significant on the capacitance. From Fig. 7c, the non-parallel line states that the

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(a)



Fig. 7. Pareto graph of standardized effects with capacitance in response to = 0.05. Graph (a) the main effect and (b) the interaction of variables on the capacitance of activated carbon-based supercapacitors.

doping type only affects the relationship between impregnation time and capacitance. The highest capacitance was achieved with urea doping at an impregnation time of 2 h and a doping ratio of 3.

The highest capacitance of modified activated carbon-based supercapacitor cells for each type of doping was ACU13-2 (43.25F g⁻¹) > ACA13-2 (34.64F g⁻¹) > ACT13-2 (33.78F g⁻¹). ACA13-2 and ACT13-2, with higher N and S content, showed lower capacitance than ACU13-2 because the higher N and S content caused oxygen. Oxygen vacancies are filled with impurity states, suppressing capacitance behavior [30[29,30]. The highest capacitance value of ACU13-2 is a compromise parameter of specific surface area (445.18 m² g⁻¹), nitrogen atom content (9.62%), and conductivity. Therefore, ACU13-2 is more suitable for electrode supercapacitor applications.

4. Conclusions

A novel N-rich-activated carbon was successfully created using the hydrothermal and activation procedures with urea, APS, and thiourea doping. The impregnation time and doping ratio significantly affect increasing the product yield. The highest result for each doping type was 38.75% (ACU13-2), 39.97% (ACT13-2), and 38.53% (ACA13-2), respectively. The single main parameter and the interaction between impregnation time with the doping type significantly affect the surface area of activated carbon. Heteroatom doping increases the surface area, but increasing the doping ratio decreases the product's surface area. The largest surface area was 677.44 m² g⁻¹ achieved for the ACA11-2 sample.

The increase in the doping ratio increases the N atomic content in the modified activated carbon. The highest N atomic content for each doping type was 9.62% (ACU13-2), 19.49% (ACT13-2), and 21.63% (ACA13-2). The impregnation time, ratio, and doping type significantly affect the specific capacitance. The highest capacitance of the supercapacitor cell of 43.22F g⁻¹ was obtained for the ACU13-2 sample. The highest capacitance was achieved from the compromise of surface area, nitrogen content, and conductivity with 445.18 m² g⁻¹ and 9.62% N, respectively. The durability test of ACU13-2 was conducted for five thousand cycles and showed that the supercapacitor cells were stable at 98.7%.

CRediT authorship contribution statement

Heri Rustamaji: Visualization, Writing – original draft, Data curation, Investigation, Methodology, Formal analysis. Tirto Prakoso: Funding acquisition, Supervision, Writing – review & editing, Data curation, Resources, Formal analysis, Conceptualization. Hary Devianto: Supervision, Writing – review & editing, Data curation, Formal analysis, Conceptualization, Methodology. Pramujo Widiatmoko: Project administration, Writing – review & editing, Resources.

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Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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