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Modification of activated carbon of rice husk using HDTMA-Br (SMAC) surfactant as nitrite ion (NO$_2^-$) adsorbent

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Modification of activated carbon of rice husk using HDTMA-Br (SMAC) surfactant as nitrite ion (NO₂⁻) adsorbent

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Abstract. Surfactant modified activated carbon (SMAC) is a product resulting from the modification of activated carbon with surfactants to increase the adsorption ability of activated carbon against ions in water. Carbonization using pyrolysis at 300°C, 350°C, and 400°C. Activation of carbon was carried out in two ways, the first activation using H_3PO_4 activator, followed by heating at 410°C for 1 hour. Second, activation using H_3PO_4 followed by radiation with microwaves. The resulting activated carbon was modified with HDTMA-Br to form SMAC, then SMAC was applied for adsorption of nitrite (NO_2^-) ions. This study aimed to determine the optimum conditions for carbonization temperature, radiation time, radiation power, adsorption time of HDTMA-Br. The adsorption capacity of SMAC on nitrite ions and the adsorption process of HDTMA-Br were studied (thermodynamic data). Characterization was carried out using FTIR, SEM, and GSA. The optimum carbonization temperature was 300°C; the optimum activation was 5 minutes and 400 watts, the optimum time for HDTMA-Br adsorption was 4 hours with the adsorption capacity was 7.304 mg/g. SMAC is effective in adsorbing nitrite ions where the adsorption capacity was 0.741 mg/g, and the adsorption efficiency is 98.833%. The adsorption of HDTMA-Br on activated carbon was physical adsorption, SMAC has an $N-(CH_3)_3$ group from HDTMA-Br with a SMAC surface area of 24.173 m^2/g.

1. Introduction

Surfactant Modified Active Carbon (SMAC) is a modified activated carbon using surfactants to increase the adsorption power of activated carbon. Several researchers have conducted research on increasing the adsorption capacity of activated carbon for specific ions. Zhang *et al.* [1] have modified activated carbon with surfactants using the cationic surfactant Cetyltrimethylammonium Chloride (CTAC) to adsorb arsenate (V) in waters. It was found that the adsorption efficiency of activated carbon against arsenate (V) reached 90%. The same study was conducted by Chen *et al.* [2] to adsorb the BrO_3^- ions. The adsorption ability of surfactant modified activated carbon increased by 81.74%.

The rice husks are carbonized using a pyrolysis process. Pyrolysis is a method of combustion with less oxygen so that more carbon is produced. The pyrolysis process is good to use because the combustion temperature can be controlled, and the time required is more efficient [3]. Temperature is one of the factors that influence the results of pyrolysis. Research on the effect of carbonization temperature in making activated carbon made from rice husks has been carried out by Naqvi *et al.* [3]. The optimum temperature for making carbon using the pyrolysis method was 500°C. Carbonization temperature affects the percentage and morphology of carbon produced.

The adsorption capacity of the carbon from pyrolysis or carbonization can be increased by adding an H_3PO_4 activator. An activator's addition shows that the carbon pores are more open so that the adsorption

capacity of activated carbon increases [4]. Chemical methods can be combined by physical means, both thermally and employing microwave radiation. Microwave radiation has several advantages, where microwave radiation is directly on the biomass and the activating agent so that heating takes place faster and saves energy [5].

In this study, activated carbon was modified using a positively charged cationic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br). This treatment is expected to change activated carbon surface to be more polar and positively charged for adsorbing anions in waters, such as acrenate, nitrate, nitrite, sulfate, and others. Nitrite ion needs to be adsorbed by SMAC because nitrite has toxic properties for living things such as animals and humans. Nitrite is also often found in drinking water, especially in agricultural areas. The limit of nitrite levels allowed in drinking water is 0.33 mg/kg body weight. If animals or humans consume excessive nitrite, nitrite will enter the blood vessels and cause methemoglobinemia. This methemoglobinemia causes blue baby syndrome in which the body becomes bluish by blocking Hb from binding O_2. Besides, nitrites can also form nitrosamine compounds that cause cancer [6]. The difference between this research and the previous research is that the resulting SMAC is applied to nitrite ion [7]

2. Methods

2.1. Materials
The materials used in this study were rice husk, distilled water, bromophenol blue, phosphate buffer pH 8, chloroform p.a., 0.1 M NaOH, 60% H3PO4, surfactant HDTMA-Br, and $NaNO_2$.

2.2. Equipment
The equipment used in this research was a pyrolysis tube (pyrolyzer), furnace, glassware, 100-mesh sieve, filter paper, universal pH, Mettler AT 200 scale, Isotemp 630F oven, Shimadzu UV-i201 UV-Vis spectrophotometer, Spectrum Version 10.4.00 PerkinElmer FTIR, GSA Quantrachome Nove Gas Sorption analyzer and Thermo Scientific Phenom ProX G6 Desktop Scanning Electron Microscope.

2.3. Procedure
The rice husks were cleaned, aerated, and hydrolyzed at various temperatures of 300°C, 350°C, and 400°C for 10 minutes. The resulting carbon was activated using 60% H3PO4 and calcined at 410°C for 1 hour. Furthermore, the activated carbon formed was contacted with HDTMA-Br. From this process, the optimum carbonization temperature can be determined. This method is called the first method.

The second method was rice husk pyrolysis at the optimum temperature and time obtained in the first method. The carbon formed was activated using 60% H_3PO_4 and irradiated with microwaves for 1, 3, 5, 7, and 9 minutes, to determine the optimum radiation time, each activated carbon was contacted with HDTMA-Br at the same contact time and concentration. after obtaining the optimum radiation time, adsorption is carried out with variations in radiation power, and the power was 80, 240, 400, 640, and 800 watts. The solid formed was filtered and washed with distilled water to a constant pH. Then activated carbon was dried using an oven at 105°C for 1 hour. Furthermore, the activated carbon was mashed using a mortar and sieved with a 100-mesh sieve.

SMAC was prepared by contacting activated carbon with HDTMA-Br surfactant 300 ppm for 3, 4, 5, 6, 7 hours so that the optimum adsorption contact time is obtained. Then filtered, and the resulting filtrate was complexed using the bromophenol Blue (BPP) method. The residue in the form of SMAC was heated at 100°C for 1 hour.

SMAC was contacted with 30 ppm $NaNO_2$ solution, then stirred at low rpm for 10 minutes and left for 1 hour, then filtered. The filtrate was then complexed using the N- (1-naphthyl) ethylenediamine dihydrochloride (NED dihydrochloride) method. The complexes formed were analyzed using a UV-Vis spectrophotometer at a wavelength of 543 nm. The formula of the adsorption efficiency and adsorption capacity are:

$$\text{adsorption efficiency} = \frac{[\text{surfaktan teradsorpsi}]}{[\text{surfaktan awal}]} \text{ x } 100\%$$

$$\text{Adsorption Capacity} = \frac{[\text{surfaktan teradsorpsi}] \text{x V(adsorbat)}}{\text{W (adsorben)}}$$

3. Results and discussion

3.1. Rice husk carbonization
Rice husks were carbonized using a pyrolysis reactor for 10 minutes at 300°C, 350°C, and 400°C [3]. The carbonization process was carried out with minimal oxygen conditions so that optimal carbon was formed. In this process, organic material is decomposed through a heating process with less oxygen, where the raw material undergoes a breakdown of its chemical structure into a gas phase. The volatile content is lost to form pores [8]. The carbon produced in this process is a porous material. To increase the carbon-produced adsorption power, modification is needed by adding an activating agent to expand the surface and open the pores so that the adsorption capacity increases [9]. Siahaan *et al.* [10] stated that pyrolysis produces charcoal or carbon, tar, and gas (CO_2, H_2O, CO, CH_4, C_2H_2, C_2H_4, and C_2H_6). The carbonization process is divided into four stages: the first, at a temperature of 100-105°C, and water evaporation occurs. Second, the decomposition step of hemicellulose and cellulose into pyroglinates occurs at temperatures of 200 - 240°C. Third, at a temperature of 240-400°C, the depolymerization process stage and the C - O and C - C bonds break. Fourth, at temperatures above 400°C, the lignin begins to break down to produce tar [11].

3.2. Activation of rice husk carbon
In the activation process, it was carried out chemically and physically. Chemical activation was carried out by adding 60% H_3PO_4 [12], while for physical activation, it was carried out by heating at a high temperature of 410°C. On carbon activation, H_3PO_4 undergoes ionization to become PO_4^{3-} which later plays a role in connecting carbon biopolymer fragments through phosphate bonds [13]. This process aims to open carbon pores and increase the surface area of the carbon. The P=O bond from the addition of phosphate acid was detected in the presence of a peak in the FTIR spectra (figure 5).

3.3. Preparation of SMAC using HDTMA-Br cationic surfactant
The preparation of SMAC was carried out by contacting the activated carbon with surfactant HDTMA-Br. The addition of 300 ppm HDTMA-Br surfactant solution was carried out on activated carbon prepared by carbonization at 300°C, 350°C, and 400°C, the activation of carbon using H_3PO_4 activator, followed by heating at 410°C for 1 hour (the fist method). The results of the adsorption efficiency and adsorption capacity of SMAC are presented in Table 1.

Table 1. The capacity and adsorption efficiency of HDTMA-Br by activated carbon prepared by carbonization temperature variations

| Sample	Ash content (%)	HDTMA-Br concentration adsorbed (ppm)	Adsorption efficiency (%)	Adsorption capacity (%)
KA-300	63.51	299.11	99.70	7.48
KA-350	60.19	298.28	99.43	7.46
KA-400	70.41	298.11	99.37	7.45

Description: KA-300, KA-350, and KA-400 are activated carbons carbonized at 300°C, 350°C, and 400°C, respectively

Table 1 shows that activated carbon obtained from carbonization at 300°C has an adsorbed HDTMA-Br concentration, adsorption efficiency, and adsorption capacity gives the best results. However, the ash

content of the KA-300 is 3.32% higher than that of the KA-350. The higher the carbonization temperature, the higher the ash content and the less carbon is obtained. Meanwhile, the smaller the amount of carbon, the smaller the HDTMA-Br concentration adsorbed. Although the differences in efficiency and adsorption capacity were not significant but carbonization at 300°C gave both measurement are highest, in terms of energy used, the lowest.

3.4. Determination of optimal time and power
The next carbon activation is carried out with microwave radiation assistance to make the activation process easier and more efficient. Determination of the optimum microwave radiation time and power can be presented in Figures 1 and 2.
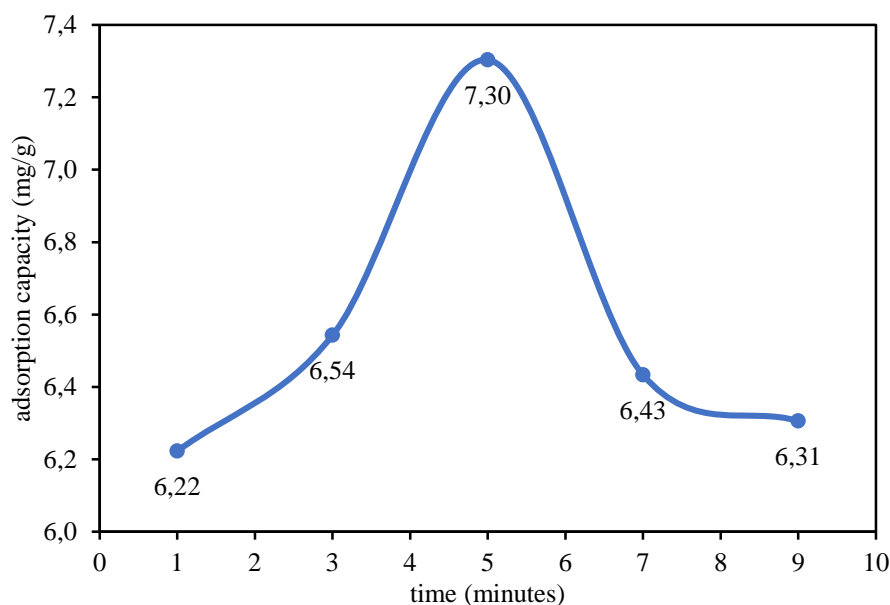
Figure 1. The relationship between radiation time and adsorption capacity

Figure 1 shows that the optimum activation time is 5 minutes, with an adsorption capacity of 7.304 mg/g. The optimum activation is based on the large, activated carbon adsorption capacity. The higher the adsorption capacity of activated carbon, the greater the amount of surfactant absorbed. At that time, the interactions between carbon and activating agents become more frequent, resulting in the opening of previously inaccessible pores [5, 14]. The adsorption efficiency above 5 minutes decreases because carbon is irradiated for a long time, it is predicted that the activated carbon will be damaged and the pores are also damaged so that the adsorption capacity will decrease and the carbon which is expected to adsorb HDTMA-Br has turned into ash.

Figure 2 shows that the optimum power obtained is 400 Watt, with a capacity of 7.304 mg/g. In microwave radiation of 80 and 400 W, the adsorption absorption is increased drastically, possibly due to the volumetric heating effect, i.e., heating the solution entirely from microwave radiation. This heating causes the pore size to expand so that the active site availability in activated carbon increases as well. The microwave radiation power of 600 and 800 W allows the formation of excess gas. This process has an adverse impact, with a reduction in surface area and porosity, so absorption and adsorption results are reduced [14, because the gas will be an impurity that occupies the pore. High radiation power may cause the pores to be damaged so that the adsorption efficiency is reduced. The resulting adsorption capacity is not much different from the first method (table 1), which uses high energy and a long time, this is the advantage of the second method using microwave radiation
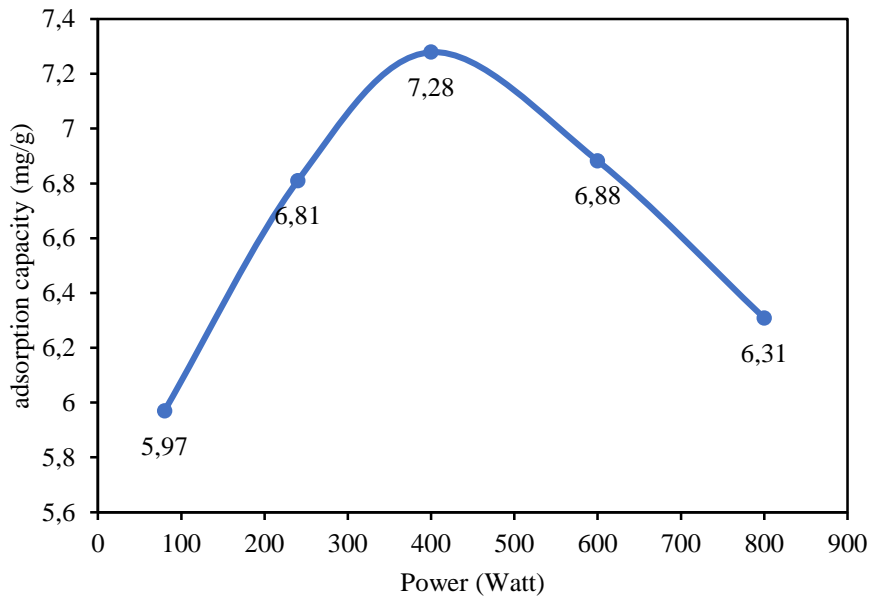
Figure 2. The relationship between radiation power and adsorption capacity

3.5. Determination of the optimum time of HDTMA-Br in SMAC preparations

SMAC preparation of activated carbon with HDTMA-Br was influenced by the contact time between activated carbon and HDTMA-Br and the concentration of HDTMA-Br. The effect of contact time and HDTMA-Br concentration on the adsorption ability is presented in Figures 3.
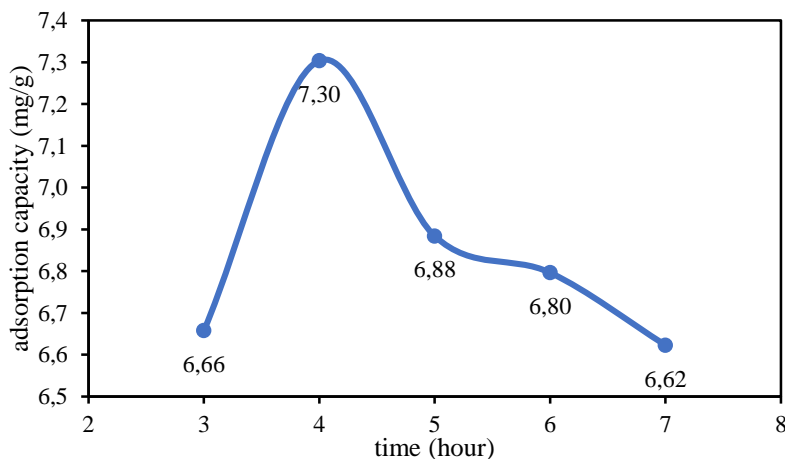

Figure 3. Relationship between contact time and adsorption capacity

Figure 3 shows that the contact time's adsorption capacity from 3 to 4 hours increases from 6.658 mg/g to 7.304 mg/g. The longer the contact time, the more HDTMA-Br that covered the activated carbon surface, and the optimum contact time was obtained at 4 hours. Meanwhile, after 4 hours, the adsorbed HDTMA-Br decreased in capacity. It is estimated that there is desorption between activated carbon and HDTMA-Br because the interaction between the active site of the adsorbent and HDTMA-Br is weakened due to the long interaction time. The surface of the activated carbon that has adsorbed will be full of HDTMA-Br molecules so that the HDTMA-Br concentration on the surface of the activated carbon is greater than the solution and it is estimated that diffusion or release of HDTMA-Br molecules from the surface of the activated carbon is expected. The surface of activated carbon covered by

HDTMA-Br is a multilayer (not monolayer of Langmuir adsorption) so that it is easily released or desorbed.

3.6. Characterization by Fourier Transfer Infra-Red (FTIR)

The characterization is done to prove whether SMAC has been formed. Carbon activated carbon, and SMAC samples were characterized using Fourier Transfer Infra-Red (FTIR). FTIR is used to analyze surface chemistry by detecting functional groups present in the sample [15]. The results of characterization using FTIR are presented in Figure 4.
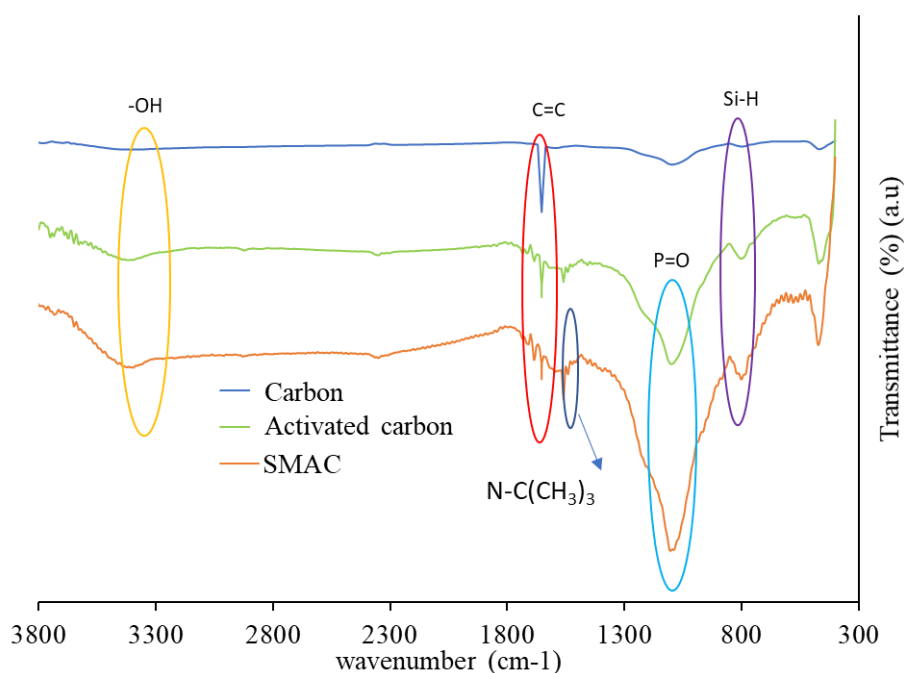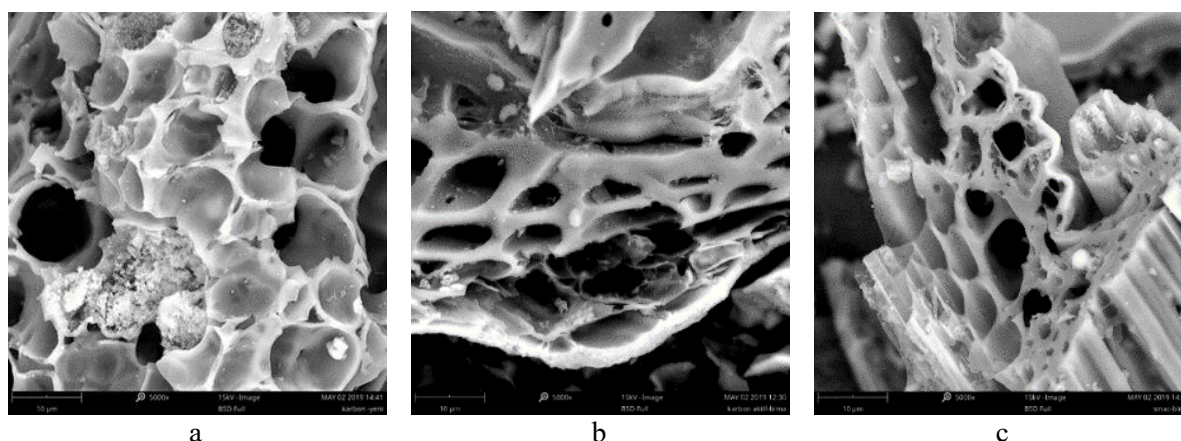

Figure 4. FTIR analysis results on carbon, activated carbon, and SMAC

Figure 4 shows the three samples of carbon, activated carbon, and SMAC show a peak in the area of wave number 3400 cm^{-1}, which is the absorption area for O-H. All samples also show a peak in the wavenumber area of about 1600 cm^{-1}, the C = C absorption area [16]. In the carbon sample, after undergoing the activation process with H_3PO_4, a P = O peak appeared, which was the phosphate group's peak. Meanwhile, at SMAC, an N-C group from N-$(CH_3)_3$ appears at a wavenumber of 1500 cm^{-1}, which comes from the addition of surfactants [17]. The N-$(CH_3)_3$ functional group shows that SMAC has been formed and it is also proven that the adsorption capacity of HDTMA-Br by activated carbon is 7.3 mg / g (Figure 3).

3.7. Characterization by Scanning Electron Microscope (SEM)

SEM analysis shows that carbon has the smallest pore for the same magnification, while the pore of activated carbon is larger than carbon. SMAC shows the largest pores. The pore radius of carbon is around 3.82-6.85 μm, activated carbon is around 4.12-8.97 μm, while SMAC is around 5.11-15.3 μm. The carbon pores are still partially covered by dirt, while the activated carbon pores are clean. The surface morphology of carbon activated carbon and SMAC can be seen in Figure 5. This shows that HDTMA-Br molecules are already attached to the surface of the activated carbon so that the SMAC surface area decrease (table 2) so that it is able to adsorb nitrite ions, electrostatic interactions occur. (table 4).

Figure 5. SEM analysis results on carbon (a), activated carbon (b), and SMAC (c)

3.8. Characterization by Surface Area Analyzer

Surface Area Analyzer is used to measure surface area. The method of calculating the surface area and pore volume in this study uses the Brunauer-Emmett-Teller (BET) method. The results of the surface area and pore volume analysis are presented in Table 2.

Table 2. Surface area, pore volume and pore radius of carbon, activated carbon, and SMAC

Samples	Surface area (m^2/g)	Pore volume (cc/g)	Pore radius (Å)
Carbon	10.094	0.012	15.571
Activated carbon	36.384	0.038	15.996
SMAC	24.173	0.014	18.472

The BET analysis (table 2) shows that activated carbon surface area is 36.384 m^2/gram, an increase of about 3.6 times from before activation, which is 10.094 m^2/gram. Meanwhile, the pore volume increased by 3.17 times after activation, from only 0.012 cm^3/gram to 0.038 cm^3/gram samples. This result is the effect of H_3PO_4, which can clean the carbon surface from the residues formed in the carbonization process. Phosphoric acid can open pores and increase the surface area [18].

The surface area and pore volume of SMAC decreased compared to activated carbon, it is possible that some HDTMA-Br molecules covered not only the surface but also the pores of the activated carbon. SMAC also has a larger surface area and pore volume than carbon, so that it can be a better adsorbent and is specific for the adsorption of anionic ions in waters such as nitrite ions (NO^{2-}).

3.9. Thermodynamics of the SMAC preparation

Thermodynamic studies were only carried out on SMAC but not on carbon and activated carbon. Thermodynamic studies need to be carried out because it can provide an idea that preparing SMAC, whether it is an exothermic or endothermic process, is spontaneous or non-spontaneous and to determine the adsorption process that occurs whether physical or chemical adsorption. Thermodynamic calculations are presented in table 3.

Table 3 represents the negative value of $\Delta G°$, which indicates the spontaneous formation of the adsorbed species thermodynamically. Enthalpy negative value indicates the exothermic property of adsorption ($-\Delta H°$). The value of ΔH is -4.3503 kJmol^{-1}, indicating the interaction between the HDTMA-Br surfactant with physically activated carbon (ΔH is 4 - 40 kJmol^{-1}). Meanwhile, the negative value of entropy ($-\Delta S°$) shows low irregularity [19].

On the other hand, the exothermic nature of the SMAC adsorption system has negative entropy ($-\Delta S°$). This means that there is a decrease in irregularity at the solid/liquid system interface due to the

mobility of the ions in the solution due to the influence of the temperature increase so that the adsorption process runs spontaneously.

Table 3. Thermodynamic Parameter Values

Temperature (K)	Thermodynamic Parameter		
	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/mol)
303	-6873.55		
313	-6964.78		
323	-7082.15	-4350.3	-22.301
333	-7153.14		
343	-7193.3		

3.10.   Nitrite (NO_2^-) Adsorption

Surfactant modified activated carbon (SMAC) was applied to adsorb nitrite anions, where the initial concentration of nitrite ions in contact with SMAC was 30 ppm. The adsorption results are presented in Table 4.

Table 4. Adsorption of nitrite ions by SMAC

Adsorbent	Residual Nitrite Concentration (mg/L)	Adsorption Capacity (mg/g)	Efficiency (%)
Carbon	4.573	0.636	84.757
Activated carbon	2.748	0.681	90.84
SMAC	0.351	0.741	98.83

Table 2 shows that the nitrite anion adsorbed by SMAC is about 8% higher than that of activated carbon. This shows the function of HDTMA-Br, which changes the activated carbon's surface to be positively charged so that the nitrite anion can be adsorbed on the SMAC positive charge. Carbon, activated carbon, and SMAC can adsorb nitrite anions because these three samples have pores where nitrite anions can infiltrate into these pores

4. Conclusion

Based on this research, it can be concluded that the optimum time and power of carbon activation were achieved in 5 minutes and 400 Watts, the optimum time of adsorption for 4 hours with a capacity of 7.30 mg/g for making SMAC. The characterization with FTIR shows the presence of functional group $N\text{-}(CH_3)_3$ on SMAC. The thermodynamic data shows a negative value of ΔG°, which indicates that the reaction was spontaneous. Meanwhile, a negative value of ΔH° indicates the reaction is exothermic and physical adsorption. Meanwhile, a negative value of ΔS° indicates a decrease in entropy. Characterization showed that the surface area and pore volume at SMAC were 24.173 m^2/g and 0.014 mL/g. Nitrite adsorption with SMAC obtained the highest adsorption capacity of 0.74 mg/g, with an efficiency of 98.83%.

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