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Modification of Activated Carbon from Rice Husk using Hexadecyltrimethylammonium Bromide (HDTMA-Br) Surfactant and $ZnCl_2$ activator and Microwaves for Nitrate Ion Adsorption

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Abstract

Surfactant Modified Activated Carbon (SMAC) is a surfactant-modified activated carbon product. The surfactant used in this study was the cationic surfactant Hexadecyltrimethylammonium Bromide (HDTMA-Br). These surfactants can change the activated carbon's surface to be positively charged due to the presence of the surfactant hydrophilic groups. This SMAC is more selective in absorbing anions, which in this study is for the adsorption of nitrate anions. This research aims to prepare a new material that is superior to activated carbon in absorbing nitrate anions. This research was conducted in several stages. In the first stage, rice husk was carbonized through pyrolysis at 300°C for 10 minutes. In the second stage, carbon was activated using 30% $ZnCl_2$ and microwaves for 5 minutes and 400 W. The third stage was modifying activated carbon by contacting or adsorbing HDTMA-Br on activated carbon. The concentration of HDTMA-Br varied at 200-400 ppm and the adsorption time was 3-7 hours. The success of the modification was measured by the efficiency of HDTMA-Br in modifying activated carbon. This is supported by the results of the characterization of FTIR, GSA, SEM, and thermodynamic parameters. The resulting SMAC was applied for the adsorption of nitrate anions, and the results were compared to carbon and activated carbon. The results indicate that the best SMAC is formed at an optimum concentration of 300 ppm, within 4 hours, with an adsorption efficiency of 97.345%. The characterization results also show that SMAC has been formed, as evidenced by the presence of a peak at a wavenumber of about 1500 cm^{-1}, a C-N group derived from $N(CH_3)_3$ in the HDTMA-Br surfactant structure. The SMAC spectra also appeared weak peaks at the wave number 2918 cm^{-1}, which indicated the CH_2-R group stretching from the HDTMA-Br surfactant. SEM image shows that HDTMA-Br has covered the pores of activated carbon. Meanwhile, the SMAC surface area is lower than that of activated carbon. Thermodynamic parameters indicate that HDTMA-Br interacts physically with activated carbon. The adsorption capacity of nitrate anion by SMAC is 3,638 mg/g, higher than carbon and activated carbon.

1. Introduction

Surfactant Modified Activated Carbon (SMAC) is a product resulting from activated carbon modification with anionic, cationic, or zwitterionic surfactants. Activated carbon modified using cationic surfactants such as hexadecyltrimethylammonium bromide (HDTMA-Br) increases its effectiveness in removing anionic pollutants [1]. Activated carbon is a porous material composed of carbon with an increased surface and pore area in an activator's presence. So this makes it possible for activated carbon to be used as an adsorbent [2]. Chen *et al.*

[3] researched increasing the adsorption capacity of activated carbon for the adsorption of specific ions who modified activated carbon with cationic surfactant Cetyltrimethylammonium Chloride (CTAC) for adsorption of BrO_3^- ions. The results showed that the adsorption ability of surfactant modified activated carbon increased by 81.74%. Pargiman *et al.* [4] modified activated carbon of rice husk using HDTMA-Br surfactant at a higher concentration of micellar critical concentration (CMC) and activator H_2SO_4 for carbon activation.

SMAC was made from rice husk through three stages. The first stage is the carbonization of rice husks. Carbonization can be carried out by the pyrolysis method with controlled combustion temperatures so that it is stable, and the time required is more efficient [5]. The second stage is the activation. Activation can be carried out in two ways, namely the chemical method and the physical method. One of the activators that can be used in the synthesis of activated carbon is $ZnCl_2$. $ZnCl_2$ in the chemical activation process functions as Lewis acid, which can bind impurities or volatile compounds left over from the carbonization process [6]. Physical activation can be done using microwaves. Microwave heating has several advantages: microwave radiation takes place on biomass and the activation agent so that heating and temperature increases take place faster, the process is more energy-efficient, and has high efficiency [7]. The third step is contacting the activated carbon with the HDTMA-Br surfactant to produce SMAC. The SMAC obtained was applied for the adsorption of nitrate anions.

This research aims to make a product that is superior to activated carbon. The efficiency of HDTMA-Br in modifying activated carbon was studied, supported by FTIR, GSA, SEM, and thermodynamic parameters characterization. The optimal concentration of HDTMA-Br and contact time of HDTMA-Br with activated carbon were also studied to obtain the best SMAC for adsorbing nitrate anions. This study used different activators during carbon activation, as well as different HDTMA-Br concentrations and contact times because the activated carbon produced was different and had not been applied for the adsorption of nitrate anions.

2. Methodology

2.1. Tools and Materials

The tools used were laboratory standard glassware, Mettler AT 200 scales, filter paper, pH meter, pyrolysis reactor, Electrolux microwave, Isotemp 630F oven, Shimadzu UV-1201 UV-Vis spectrophotometer, 100-mesh sieve, Whatman filter paper, thermometer, Perkin Elmer Spectrum Version 10.4.00 Fourier transform infrared spectroscopy (FTIR), Phenom Pro-X and GSA Quantachrome AsiQwin 3.01 scanning electron microscope (SEM). The materials used were rice husk, HDTMA-Br surfactant, distilled water, bromophenol blue, $ZnCl_2$, 0.1 M NaOH, pH 8 phosphate buffer, KNO_3 solution, and chloroform. All materials used in this study were analytical grade reagents.

2.2. Modifying activated carbon with HDTMA-Br

400 g rice husks, which have been washed and dried by aerating, were carbonized using a pyrolysis apparatus for 10 minutes at 300°C. The resulting carbon was put into a 30% $ZnCl_2$ solution then irradiated using microwaves at 400 W for 5 minutes. The activated carbon was contacted with HDTMA-Br surfactant at various concentrations (200, 250, 300, 350, 400 ppm) and variations in contact time (3, 4, 5, 6, 7 hours). Each sample variation was filtered, the residue was dried then stored. The filtered filtrate was complexed with Bromophenol Blue, and then the absorbance was measured using a UV-Vis spectrophotometer at a wavelength of 606 nm. The resulting SMAC was characterized by FTIR, SEM, GSA, and thermodynamic data.

2.3. Nitrate Ion Adsorption

Nitrate ion adsorption was carried out by inserting carbon, activated carbon, and SMAC samples into a 150 ppm KNO_3 solution [8] and then allowed to stand for 1 hour. Filtering was carried out to obtain the filtrate, and then the nitrate ion concentration was analyzed using the American Public Health Association (APHA) method. The APHA method was carried out by adding a solution of HCl to the sample and stirring. The nitrate absorbance was read using a UV-Vis spectrophotometer at a wavelength of 220 nm and 275 nm to determine the disturbance due to dissolved organic matter.

2.4. Determining Thermodynamic Parameters

Activated carbon under optimum conditions was contacted with 300 ppm HDTMA-Br surfactant for 4 hours with temperature variations (30, 40, 50, 60, 70°C). Then, each sample variation was filtered to separate the residue and the filtrate. The separated residue was dried then stored, while the filtrate was complexed with Bromophenol Blue. The absorbance of the complex formed was measured using a UV-Vis spectrophotometer at a wavelength of 606 nm.

3. Results and Discussion

400 g of dry rice husk is carbonized using a pyrolysis device at a temperature of 300°C for 10 minutes, resulting in a total of 147.07 g. Activation of rice husk carbon is carried out chemically and physically. Chemical activation was carried out by adding 30% $ZnCl_2$, while physical activation was carried out using microwave radiation. 1 g of carbon produces 0.91 g of activated carbon.

3.1. Modifying Activated Carbon with Surfactant HDTMA-Br

Adsorption of HDTMA-Br surfactant by activated carbon was carried out to obtain SMAC, which could increase its ability as an adsorbent. As much as 1 g of activated carbon contacted with HDTMA-Br at optimum conditions produced 0.86 g of SMAC. The interaction between activated carbon and HDTMA-Br surfactant is illustrated in Figure 1.

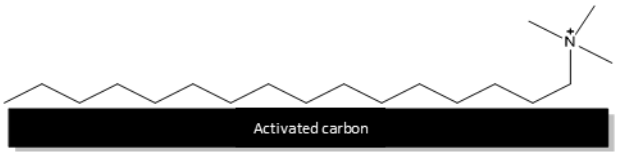


Figure 1. Hydrophobic interaction between activated carbon and HDTMA-Br surfactant [9]

3.1.1. Determination of the Optimum HDTMA-Br Concentration on Activated Carbon Modification

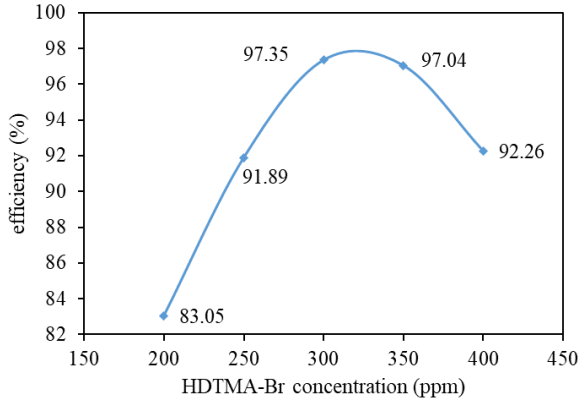


Figure 2. Effect of HDTMA-Br surfactant concentration on the adsorption efficiency of HDTMA-Br surfactant

The results of determining the optimum HDTMA-Br concentration are shown in Figure 2. The efficiency of HDTMA-Br that modifies activated carbon at a concentration of 200 to 300 ppm has increased. In other words, increasing the concentration of HDTMA-Br surfactant causes an increase in the amount of HDTMA-Br surfactant that interacts with activated carbon. This interaction is caused by adsorption. However, at higher concentrations, which were at 400 and 500 ppm, efficiency decreased. It is estimated that the activated carbon surface pores have been closed by the HDTMA-Br surfactant so that its adsorption has reached a saturation point and HDTMA-Br is re-desorption.

3.1.2. Determination of the Optimal Contact Time on Activated Carbon Modification

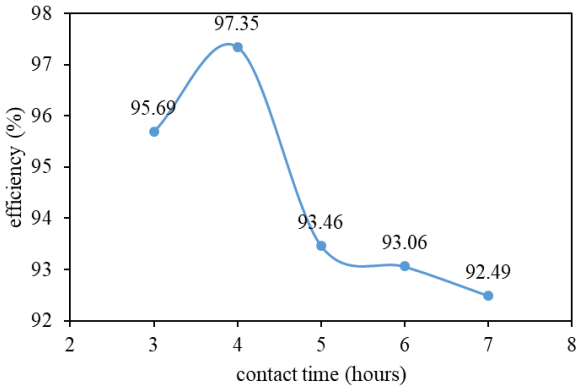


Figure 3. Effect of contact time on the efficiency of the HDTMA-Br surfactant

The results of determining the optimum contact time are shown in Figure 3. The highest efficiency of HDTMA-Br in modifying activated carbon is at the contact time of 4 hours. Efficiency at a contact time of 3 to 4 hours has increased. This shows that the interaction between adsorbent and adsorbate increases with the more extended collision between the HDTMA-Br surfactant and the activated carbon. Meanwhile, the contact time that exceeds 4 hours shows a decreasing efficiency. This is because HDTMA-Br has saturated the pore surface of the activated carbon.

3.2. Fourier Transform Infrared Spectroscopy

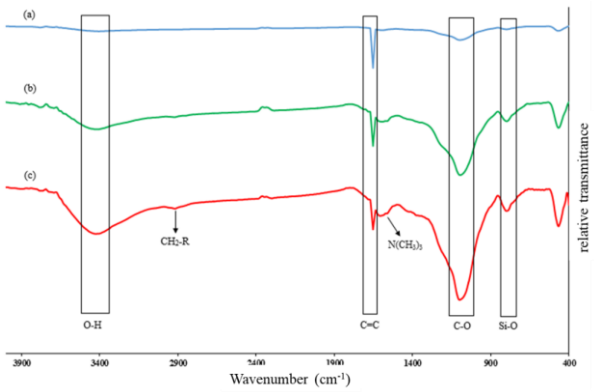
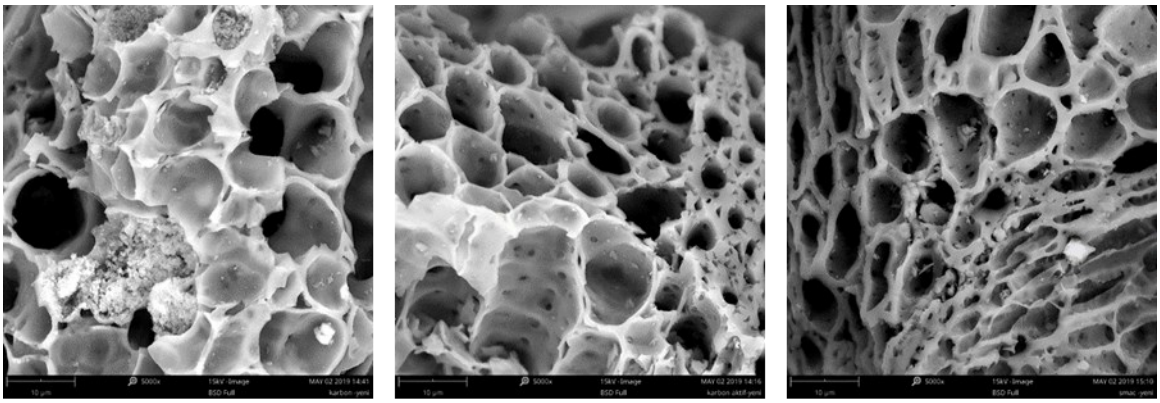


Figure 4. FTIR spectra of (a) carbon, (b) activated carbon, and (c) SMAC

Figure 4 shows that the SMAC spectra contain a weak peak at the wave number 1504 cm^{-1}. This is according to [4], which showed a peak at the wavenumber of about 1500 cm-1, which was the C-N group of N (CH3) 3 in the HDTMA-Br surfactant. The SMAC spectra also showed a weak peak at the wave number 2918 cm^{-1}, derived from the stretching vibration of CH_2-R originating from the HDTMA-Br surfactant [10]. Other peaks that are not much different from activated carbon and carbon, such as the wavenumber peaks between 3405-3414 cm^{-1}, indicate the O-H group. The group C = C appears in the wavenumber between 1653-1658 cm^{-1}. The C-O groups appear at the wavenumbers between 1095-1099 cm^{-1}, while the Si-O groups in the spectra of all samples appear at wavenumbers between 794-799 cm^{-1}.

3.3. Scanning Electron Microscope

Figure 5 shows SEM analysis results, which show that the pores of carbon are still closed while the pores of activated carbon are clean. $ZnCl_2$ activator and microwave radiation can clean the pores from impurities such as residual carbonization. SEM image from SMAC shows that some of the pores are filled with material estimated by HDTMA-Br. This is following [4], which shows that SMAC's pore volume is slightly smaller than that of activated carbon because some HDTMA-Br surfactant molecules cover its surface. The SEM results are in accordance with the SMAC FTIR data, which gave rise to the peaks estimated to be from HDTMA-Br.



carbon Activated carbon SMAC

Figure 5. The surface morphology of carbon, activated carbon, and SMAC, analyzed using SEM with a magnification of 5000x

3.4. Gas Sorption Analyzer

Table 1. Surface area, pore-volume, and pore diameter of carbon, activated carbon, and SMAC

Samples	Surface area (m^2/g)	Pore volume (mL/g)	Pore radius (Å)
Carbon	10.094	0.012	15.571
Activated carbon	12.120	0.021	15.049
SMAC	7.091	0.018	16.142

Table 1 shows that the surface area and pore volume of carbon increased after being activated using $ZnCl_2$. This is because the activator can bind impurities on the carbon surface of the carbonization process [11]. The large pore volume and surface area of activated carbon make it possible to increase the adsorption ability of large molecules such as the HDTMA-Br surfactant, whose molecular weight is 364.45 g/mol [12]. GSA analysis results on SMAC show that the surface area and pore volume have decreased compared to activated carbon. This is due to some HDTMA-Br surfactant molecules that enter the pores so that they cover part of the surface of the activated carbon. These results are in line with the FTIR and SEM data from SMAC. However, the blocking of SMAC by HDTMA-Br had a positive impact because the SMAC obtained tended to be cationic, thus increasing the adsorption ability of anionic pollutants such as nitrate ions.

Figure 6 shows that the adsorption isotherm curve is not the same as that of desorption. This indicates hysteresis, in which the adsorption process results in gas condensation in ink bottle-shaped pores [13]. This proves that some of the pores of SMAC are shaped like ink bottles.

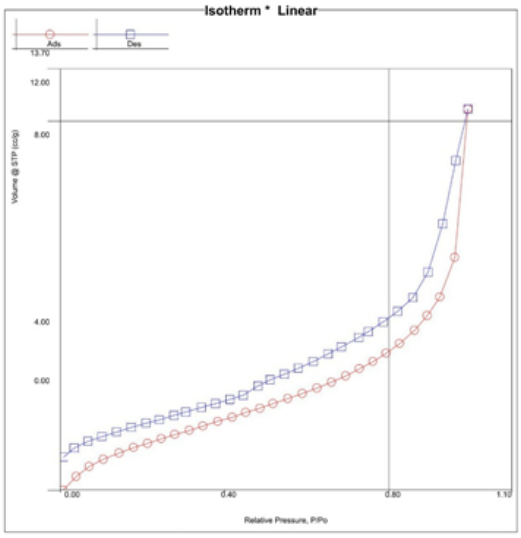


Figure 6. SMAC adsorption isotherm

3.5. Thermodynamic Parameters

Thermodynamics of HDTMA-Br surfactant adsorption by activated carbon studied the parameters of Gibbs free energy (ΔG), entropy (ΔS), and enthalpy (ΔH), which can be calculated by the equation [14]:

$$\Delta G = \Delta H - T\,\Delta S \quad (1)$$

These thermodynamic parameters can be determined by constructing the ln K versus 1/T curve.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R}\frac{1}{T} \quad (2)$$

Table 2. Thermodynamic parameters of the interaction between HDTMA-Br surfactants and activated carbon

T (K)	ΔH (J/mol)	ΔS (J/ K mol)	ΔG (J/mol)
303			-7540.17
313			-7413.39
323	-11381.87	-12.68	-7286.6
333			-7159.81
343			-7033.02

Table 2 explains the thermodynamic parameter information to estimate the interaction of HDTMA-Br

surfactants with activated carbon. The value of ΔH is -11.381 kJ.mol^{-1}, which indicates that the interaction between HDTMA-Br surfactant and activated carbon is physical or physical ((H is 4 - 40 kJ.mol^{-1}). The negative sign indicates that the HDTMA-Br surfactant adsorption process on activated carbon was exothermic. The negative value of ΔG indicates that the process is spontaneous. At the same time, ΔS is negative, indicating a decrease in the irregularity of the adsorbate and adsorbent interfaces during the adsorption process [15].

3.6. Nitrate Ion Adsorption

The adsorption of nitrate ions by SMAC is shown in Figure 7, as measured by the adsorption capacity. The adsorption capacity of nitrate ion by SMAC is 3,638 mg/g, more significant than carbon and activated carbon. This shows that there is an effect of the hydrophilic group charge HDTMA-Br. Adsorption occurs due to electrostatic interactions on the SMAC surface [16]. Carbon and activated carbon can also adsorb nitrate ions, but not as a result of charge interactions. Adsorption on carbon and activated carbon comes from the pores, where nitrate ions are absorbed in the pores on the external and internal surfaces.

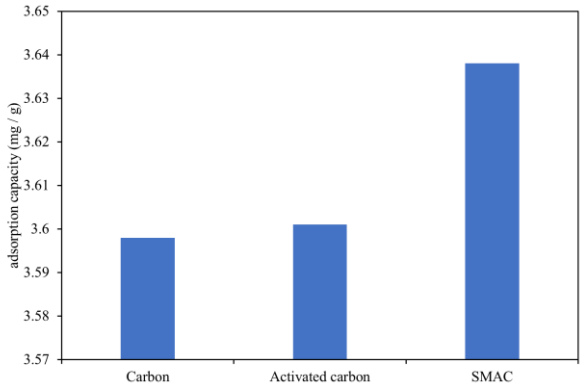


Figure 7. The adsorption capacity of nitrate ions by carbon, activated carbon, and SMAC

4. Conclusion

Modification of activated carbon with surfactants (SMAC) has been successfully carried out with optimum results at a concentration of HDTMA-Br 300 ppm and a time of 4 hours. FTIR analysis of SMAC proved that the -$N(CH_3)_3$ group was derived from the HDTMA-Br surfactant. Activated carbon pores filled with HDTMA-Br. The surface area and pore volume are reduced, and the interaction between HDTMA-Br and activated carbon is physical interaction. SMAC can adsorb nitrate ions with an adsorption capacity of 3.638 mg/g, higher than activated carbon and carbon.

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