# Jurnal Kimia Sains dan Aplikasi
## Journal of Scientific and Applied Chemistry

# Synthesis of Surfactant-Modified Activated Carbon (SMAC) Above Critical Micelle Concentration as Cr(VI) Ion Adsorbent

Arnelli [a,*], Sri Guswini [a], Ahmad Suseno [a]

[a] Chemistry Department, Faculty of Science and Mathematics, Diponegoro University, Prof. Soedarto S.H., Tembalang, Semarang, Central Java, Indonesia, 50275

*Corresponding author: arnelli@live.undip.ac.id

## Article Info

## Abstract

The synthesis of surfactant-modified activated carbon (SMAC) has been widely studied. However, no research has been conducted to study SMAC concentrations higher than the critical micellar concentration. Therefore, in this study, SMAC was synthesized using anionic and cationic surfactants above CMC (Critical Micelle Concentration) and compared with SMAC below CMC and coconut husk-based activated carbon. This study aimed to determine the surface profile of SMAC and the characteristics and mechanism of metal ion adsorption by SMAC. The selected metal ions were Cr(VI) cations and $NH_4^+$ cations as a reference. SMAC was prepared by modifying coconut shell-based activated carbon with anionic surfactant SLS (Sodium Lauryl Sulfate) and cationic surfactant HDTMA-Br (Hexadecyl Trimethyl Ammonium Bromide). Modification of SMAC was performed by three different methods: (a) activated carbon was added gradually with SLS followed by HDTMA-Br, (b) activated carbon was added with HDTMA-Br followed by SLS, (c) activated carbon was mixed with SLS and HDTMA-Br simultaneously. All synthesized SMAC were characterized using FTIR, GSA (Gas Sorption Analyzer), and zeta potential. The FTIR analysis results showed that the synthesized SMAC comprised S=O and $(CH_3)_3N^+$ groups derived from surfactants. GSA analysis revealed that SMAC has a surface area of 36.790 m²/g, and it was more stable than activated carbon according to the zeta potential result. In this study, the efficiency of SLS and HDTMA-Br in synthesizing SMAC was 99.98% and 95.85%, respectively. SMAC synthesis using method c resulted in Cr(VI) adsorption efficiency of 93.50% and $NH_4^+$ adsorption efficiency of 87.37%. In comparison, SMAC below CMC has adsorption capacities of 93.41% for Cr(VI) and 85.05% for $NH_4^+$, respectively, whereas Cr(VI) adsorption efficiency by coconut shell-based activated carbon was 99.98%.

## 1. Introduction

Surfactant-modified activated carbon (SMAC) can be synthesized from activated carbon and surfactant, substantially increasing the efficiency and adsorption capacity for toxic pollutants compared to regular carbon [1]. The profitable coconut shells are utilized to produce activated carbon in this study because they have a higher density and purity level, are harder, and are nearly ash-free [2]. The surfactants used are cationic, anionic, and non-ionic surfactants [3]. Several studies have investigated the use of surfactants to modify activated carbon, such as Lee *et al.* [3]. The result revealed that using anionic surfactants such as sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), and sodium octanoate (SO), an 82% ammonium ion adsorption efficiency was able to achieve. Modification of activated carbon from Lamtoro using cationic surfactant Hexadecyltrimethylammonium Bromide (HDTMA-Br) could increase the adsorption capacity of Cr(VI) ions by 3.29 mg/g [4]. According to Agustinus *et al.* [5], the adsorption capacity of coal-based activated carbon to Cr(VI) metal ions can be increased twice

through modification with cationic surfactant Ethylinediamine, ranging from 52.09% to 100%. The modification of activated carbon with SLS and (HDTMA-Br) below the CMC was studied by Arnelli *et al.* [6] to adsorb Pb cations and nitrate anions and gave adsorption capacities of 1.376 and 0.896 mg/g for cations and anions, respectively.

The initial stage in manufacturing activated carbon is to carbonize coconut shells using the pyrolysis method. Onwuka *et al.* [7] carbonized coconut shell at $400°C$ for an hour in a pyrolysis reactor. The carbon is then activated with the $ZnCl_2$ activator, which promotes the formation of new pores and increases the carbon surface area. The presence of $ZnCl_2$ inhibits tar formation and encourages aromatization, resulting in porous activated carbon [8]. The resulting pores depend on the ratio of $ZnCl_2$ added upon activation. At the concentration ratio of $ZnCl_2$:biomass (1:5), the pores formed are mostly microporous (< 2nm), while in the ratios 2:5 and 3:5, the pores are mesoporous (2–50 nm) [9].

The activation process is performed using microwave radiation since it only requires a shorter time. Furthermore, energy is transferred directly to the carbon part through molecular interactions, making it more energy-efficient [10]. Microwave has been used by Özhan *et al.* [11] to make activated carbon from spruce seeds using a $ZnCl_2$ activator and can produce activated carbon with a surface area of 939 $m^2$/g in a short time of 5 minutes.

Activated carbon was modified with cationic surfactant Hexadecyltrimethylammonium Bromide (HDTMA-Br) and anionic surfactant Sodium Lauryl Sulfate (SLS) at concentrations above the critical micelle concentration (CMC). The two surfactants were chosen for their capacity to increase the surface area of activated carbon while also changing its nature to become polar and charged. The novelty of this research is modifying activated carbon by adding surfactants above the CMC, resulting in micelles (aggregate of surfactant molecules) filling the activated carbon [12]. This is predicted to enhance metal ion adsorption.

SMAC characteristics were studied by FTIR to identify the functional groups, GSA to determine surface area and total pore volume, and zeta potential to assess particle stability. The efficiency of SLS and HDTMA-Br in SMAC was also determined. SMAC was employed for the adsorption of Cr(VI) ions and $NH_4^+$ ions as a reference.

## 2. Methodology

### 2.1. Materials

$ZnCl_2$, distilled water, Sodium Lauryl Sulfate (SLS), HDTMA-Br, coconut shell, methylene blue (analytical grade), phosphate buffer, pH 8, Bromophenol Blue (BPB) (analytical grade), $H_2SO_4$ (analytical grade), NaOH, $NaH_2PO_4.1H_2O$, phenolphthalein indicator, chloroform (analytical grade), 1,5-Diphenylcarbazide (analytical grade), sugarcane bagasse-derived activated carbon (KA 2), Nessler's reagent.

### 2.2. Equipment

Laboratory standard glassware, filter paper MN No. 42, analytical balance, aluminum foil, porcelain dish, mortar, separating funnel, 100 mesh sieve, pyrolysis reactor, 630F Isotemp oven, microwave, magnetic stirrer, UV-Vis spectrophotometer, GSA, FTIR, and zeta potential.

### 2.3. Procedure

The cleaned coconut shell was dried and carbonized in a pyrolysis reactor at $400°C$ for 10 minutes [6]. Carbon was put into a 30% $ZnCl_2$ solution and then irradiated with 400 W microwaves for 5 minutes. Activated carbon was initially contacted with each surfactant above and below the CMC to determine the efficiency of the surfactant in modifying the activated carbon before synthesizing SMAC.

SMAC synthesis was conducted in three different methods. Activated carbon was contacted with $80 \times 10^{-3}$ M SLS surfactant solution for 4 hours, then allowed to stand and filtered, and the resulting residue was dried. The dried residue was contacted with $90 \times 10^{-4}$ M HDTMA-Br surfactant solution for 4 hours (method a). Method b, the activated carbon was contacted with HDTMA-Br $90 \times 10^{-4}$ M for 4 hours, then allowed to stand and filtered. The resulting residue was then dried, and the dried residue was contacted with $80 \times 10^{-3}$ M SLS surfactant solution for 4 hours. Method c involved mixing activated carbon with surfactants HDTMA-Br $90 \times 10^{-4}$ M and SLS $80 \times 10^{-3}$ M simultaneously. For Cr(VI) adsorption, SMAC was contacted with 40 ppm Cr(VI) for 30 minutes. After adsorption, the filtrate was complexed with 1,5-Diphenylcarbazide and analyzed using a UV-Vis spectrophotometer to quantify the amount of Cr(VI) adsorbed and the adsorption efficiency. As a comparison, a 55 ppm $NH_4^+$ cation solution was also contacted with SMAC for 30 minutes. After complexing with the Nessler's reagent, $NH_4^+$ cations were analyzed using a UV-Vis spectrophotometer.

## 3. Results and Discussion

The CMC of SLS is $8 \times 10^{-3}$ M, and HDTMA-Br is $9 \times 10^{-4}$ M; hence bilayer lamellar micelles were produced at a concentration of 10xCMC [12]. The first step was contacting activated carbon with SLS surfactant at a concentration of $80 \times 10^{-3}$ M, then measuring the efficiency of SLS adsorption onto the surface of the activated carbon. The same method was conducted for HDTMA-Br at a $90 \times 10^{-4}$ M concentration and concentrations below CMC for SLS and HDTMA-Br. The results are shown in Table 1.

**Table 1.** Surfactant adsorption efficiency by activated carbon

| Surfactant | Concentration (M) | Surfactant adsorption efficiency (%) |
|---|---|---|
| SLS | $4.5 \times 10^{-3}$ | 99.78 |
| | $80 \times 10^{-3}$ | 99.98 |
| HDTMA-Br | $6.0 \times 10^{-4}$ | 80.22 |
| | $90 \times 10^{-4}$ | 95.85 |

Table 1 shows no significant difference in the efficiency of the two surfactants at low and high concentrations. At an initial $80 \times 10^{-3}$ M concentration, activated carbon could adsorb 99.98% of SLS. Meanwhile, HDTMA-Br was only able to adsorb 95.85% at an initial concentration of $90 \times 10^{-4}$ M. The efficiency difference between SLS and HDTMA-Br at a low concentration was 19.56%. The difference in results was attributed to HDTMA-Br (364.45 g/mol) having a greater molecular size than SLS (288.38 g/mol), making it more challenging for HDTMA-Br to access the activated carbon surface and pores.

Surfactants above the CMC value will form lamellar micelles (two-layer micelles) [10], and these micelles are attached to the surface of the activated carbon, illustration as shown in Figure 1b. The difference between Figure a and Figure b lies in the group of surfactants interacting with the activated carbon. In Figure 1a, the hydrophobic group of the surfactant is oriented to the activated carbon because it is still below the CMC, and micelles have not yet formed. Figure 1b shows that above CMC (10xCMC) lamellar micelles have been formed; when these micelles are contacted with activated carbon, the hydrophilic head of the surfactant searches for sites of opposite charge ($\partial$ − or +) of activated carbon [12]. Surfactant monomers interact with activated carbon by hydrophobic bonds, whereas electrostatic interactions occur in the micellar form [12].
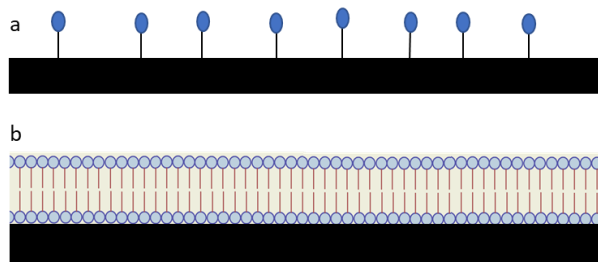


**Figure 1.** Illustration of surfactants attached to the surface of activated carbon (a) surfactants in the form of monomers (b) surfactants in the form of micelles [12]

In the next stage, SMAC was synthesized through three methods. Method a was performed by contacting activated carbon with $80 \times 10^{-3}$ M SLS solution and then allowed to stand. The residue formed was filtered and dried. The dried residue was contacted with a $90 \times 10^{-4}$ M HDTMA-Br solution (sample code: SMAC(A)). The procedure in method b (SMAC(B)) is the opposite of method a. In method c, the activated carbon was mixed with HDTMA-Br $90 \times 10^{-4}$ M and SLS $80 \times 10^{-3}$ M simultaneously, and the residue was coded as SMAC-T. For comparison, activated carbon was contacted with HDTMA-Br $6.0 \times 10^{-4}$ M and SLS $4.5 \times 10^{-3}$M (below the CMC value) simultaneously, with sample code SMAC-R. The formula used to calculate the surfactant efficiency (adsorption) is efficiency $= \frac{C_o - C_t}{C_o} x\ 100\%$, where $C_o$ is the initial surfactant concentration, and $C_t$ is the concentration after contact with activated carbon.

### 3.1. Characterization

#### 3.1.1. FTIR

FTIR spectrum analysis was used to determine the functional groups in activated carbon (KA 1), surfactant modified activated carbon SLS and HDTMA-Br at concentrations below CMC (SMAC-R) and above CMC (SMAC-T), as shown in Figure 2.
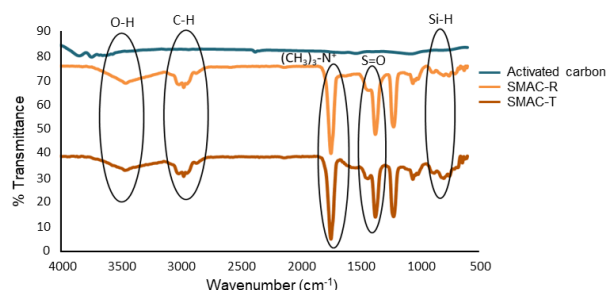


**Figure 2.** FTIR spectra of activated carbon and SMAC

The SMAC-T and SMAC-R spectra show a new absorption peak at 2974 cm$^{-1}$, indicating aliphatic sp$^3$ C−H stretching vibrations from HDTMA-Br and SLS. The absorption peak at 1700 cm$^{-1}$ indicates the stretching vibration of $(CH_3)_3$−N$^+$ from the surfactant HDTMA-Br [13]. The absorption peak is relatively weak at 1371.25 cm$^{-1}$, indicating the presence of a S=O functional group originating from the SLS surfactant [14]. This proves that SMAC has been successfully produced.

#### 3.1.2. GSA

GSA characterization was conducted on KA 1, KA 2, SMAC-R, and SMAC-T samples. The results are shown in Table 2.

**Table 2.** Surface area, pore volume, and pore diameter of activated carbon, SMAC-R, and SMAC-T

| Sample | Surface Area (m²/g) | Pore volume (cc/g) | Pore radius (Å) |
|--------|--------|--------|--------|
| KA 1 | 23.900 | 0.007 | 18.064 |
| KA 2 | 210.700 | 0.168 | 23.500 |
| SMAC-R | 35.735 | 0.033 | 15.695 |
| SMAC-T | 36.790 | 0.060 | 19.207 |

Table 2 shows that after interacting with surfactants (SMAC), the surface area, pore volume, and pore radius of activated carbon (KA 1) increase. It can be assumed that surfactants can increase surface area, pore volume, and pore radius. Surfactants can modify these three parameters because the surfactant enters the cavities of the activated carbon biopolymer layers [15]. The three parameters between SMAC-T and SMAC-R are increased slightly by approximately 2.9% due to large micelles formation in SMAC-T. The increase in surface area is assumed that the surfactant has filled between layers of activated carbon so that the distance between the activated carbon layers increases.

For Cr(VI) adsorption, sugarcane bagasse-derived activated carbon (KA 2) with a large surface area, pore volume, and pore radius was employed as a reference. Compared to Arnelli *et al.* [6], the success of this study is that the surface area increased to 36.790 m²/g while

theirs only reached 14.472 m²/g. The pore size distribution of activated carbon, SMAC-R, and SMAC-T can be seen in Figure 3, that the most significant pore enlargement is greater than 20 in diameter [16].
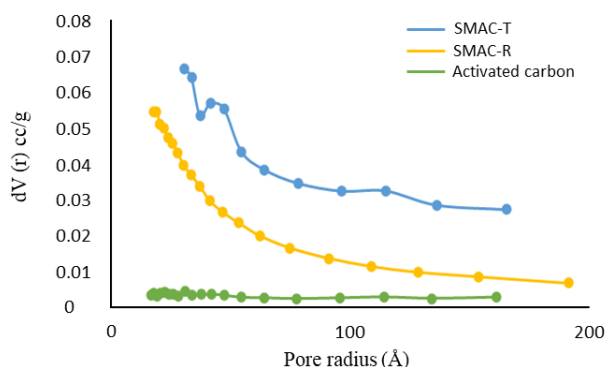


**Figure 3.** Pore distribution

### 3.1.3. Zeta Potential

Zeta potential analysis was carried out to determine particle stability. The zeta potential results on activated carbon, surfactant modified activated carbon at concentrations below CMC (SMAC-R) and above CMC (SMAC-T) can be seen in Table 3.

**Table 3.** Zeta Potential Results

| Sample | Zeta Potential (mV) |
| --- | --- |
| Activated carbon | −0.4 |
| SMAC-R | −3.8 |
| SMAC-T | −4.1 |

Table 3 shows that the zeta potential value of SMAC- T was −4.1 mV, which is more negative than activated carbon and SMAC-R. The zeta potential of activated carbon is nearly zero, which was −0.4, and SMAC-R was −3.8 mV. The adsorption of anionic-cationic surfactant molecules changes the zeta potential of activated carbon particles even at low concentrations. Changes in the zeta potential value indicate the adsorption of surfactant micelles on the activated carbon layer. The more negative the zeta potential indicates the formation of a charge (positive or negative) on the adsorbent surface, which increases the electrostatic repulsion between particles, thereby reducing particle aggregation and increasing particle stability. This impact minimizes the likelihood of particle aggregation, thereby reducing the probability of bigger aggregated particles flocculating or sedimenting [17]. SMAC-T was more stable than activated carbon and SMAC- R, evidenced by a significant zeta potential value. Increasing SMAC zeta potential from activated carbon proves activated carbon has adsorbed SLS and HDTMA-Br so that SMAC was formed.

### 3.2. Application of SMAC

### 3.2.1. Adsorption of Cr(VI)

The initial application of SMAC was to adsorb Cr(VI) ions. The three methods of manufacturing SMAC revealed that SMAC's ability to adsorb Cr(VI) was not significantly different, as shown in Figure 4.
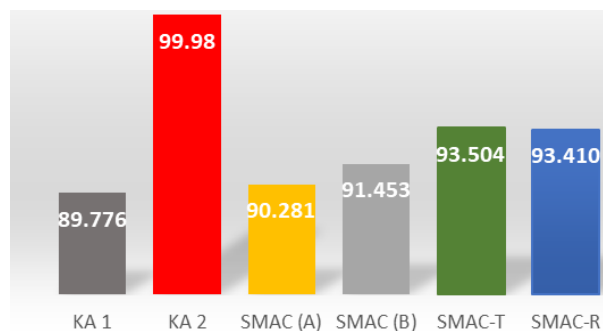


**Figure 4.** Cr(VI) adsorption efficiency

The difference in the adsorption efficiency of Cr(VI) on SMAC-T, SMAC (A), and SMAC (B) only ranged from 2−3%. This is due to all methods the SMAC surface contains negative and positive charges derived from SLS and HDTMA-Br, and in the form of micelles, as shown in Figure 1b. Cr(VI) would be adsorbed on the positively charged site of the $(CH_3)_3$-N$^+$ group (Figure 2) in the head region of the HDTMA-Br micelles because Cr(VI) was in the form of $CrO_4^{2-}$ ions. The difference in adsorption efficiency between SMAC-T and SMAC-R was only about 0.1%. It is estimated that in SMAC-R (Figure 1a), the surfactant is in the form of monomers. This monomer can reach the entire surface of the activated carbon, both the outer and inner surfaces of pores, because the most pores are at 20 Å (mesopore), as shown in Figure 3. The more surfactant molecules that interact with the surface of the activated carbon, the more charged sites are available.

Surfactants in the form of micelles can only occupy the outer surface or between layers of activated carbon. Figure 4 also shows the adsorption efficiency of Cr(VI) by KA 2 (as a reference). According to the result, the adsorption efficiency could reach 99.98%. Because of the enormous surface area of KA 2 (210.700 m²/g) (Table 2), the adsorption capacity was considerably higher. The zeta potential analysis (Table 3) proved that SMAC was more stable than activated carbon. This suggested that SMAC adsorption would be persistent and hard to remove, supported by the Cr(VI) adsorption mechanism involving electrostatic interactions [18].

### 3.2.2. Adsorption of NH₄⁺

Adsorption of NH$_4^+$ (as a reference) was used to determine the effect of charged sites on SMAC. Table 1 shows that the two surfactants can modify activated carbon at concentrations above CMC (SMAC-T) with no significant efficiency difference. The NH$_4^+$ was distributed on the negatively charged site of the SLS head group. FTIR characterization (Figure 2) proved the presence of a S=O functional group originating from the negatively charged hydrophilic SLS head. The efficiency of NH$_4^+$ adsorption on SMAC-T was 87.372% (Figure 5) because SMAC-T contained more negative charges than others.
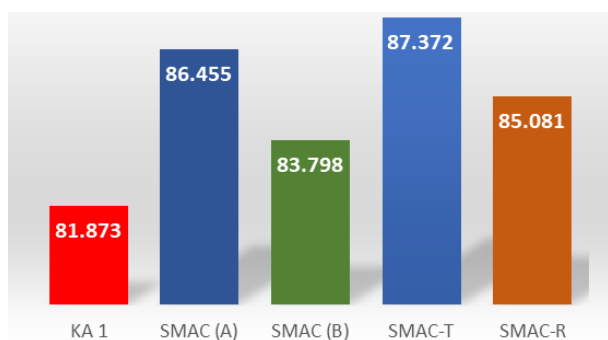
**Figure 5.** $NH_4^+$ adsorption efficiency

Figures 4 and 5 indicate only a 10% difference in Cr(VI) and $NH_4^+$ cation adsorption between SMAC-T and SMAC, implying that SMAC-T's positive and negative sites were nearly identical. Adsorption of $NH_4^+$ ions and Cr(VI) ions through the process of electrostatic interaction [18], Cr(VI) ions would be adsorbed on a positive charge and $NH_4^+$ on a negative charge.

## 4. Conclusion

SMAC has been successfully synthesized by examining the profile (the presence of specific surfactant functional groups, larger and more stable surface area), the mechanism of Cr(VI) adsorption on all SMAC through the inner surface (pores), and the outer surface containing sites charged or electrostatic interactions. The adsorption efficiency of SMAC to adsorb Cr(VI) and $NH_4^+$ was not significantly different.

## References

[1] Chi K. Ahn, Donghee Park, Seung H. Woo, Jong M. Park, Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactants, *Journal of Hazardous Materials*, 164, 2-3, (2009), 1130-1136 https://doi.org/10.1016/j.jhazmat.2008.09.036

[2] Ilknur Demiral, Canan Aydın Şamdan, Hakan Demiral, Production and characterization of activated carbons from pumpkin seed shell by chemical activation with $ZnCl_2$, *Desalination and Water Treatment*, 57, 6, (2016), 2446-2454 https://doi.org/10.1080/19443994.2015.1027276

[3] Wooram Lee, Sangwon Yoon, Jong Kwon Choe, Miran Lee, Yongju Choi, Anionic surfactant modification of activated carbon for enhancing adsorption of ammonium ion from aqueous solution, *Science of the Total Environment*, 639, (2018), 1432-1439 https://doi.org/10.1016/j.scitotenv.2018.05.250

[4] Surachai Karnjanakom, Panya Maneechakr, Adsorption behaviors and capacities of Cr (VI) onto environmentally activated carbon modified by cationic (HDTMA and DDAB) surfactants, *Journal of Molecular Structure*, 1186, (2019), 80-90 https://doi.org/10.1016/j.molstruc.2019.03.022

[5] Eko Tri Sumarnadi Agustinus, Anggoro Tri Mursito, Happy Sembiring, Peningkatan daya serap karbon aktif terhadap ion logam hexavalent chromium (CrVI) melalui modifikasi dengan cationic surfactant (ethylinediamine), *RISET Geologi dan Pertambangan*, 23, 1, (2013), 15-26 http://dx.doi.org/10.14203/risetgeotam2013.v23.66

[6] Arnelli Arnelli, Rahmatul Fazira, Yayuk Astuti, Ahmad Suseno, Synthesis of Sodium Lauryl Sulfate (SLS) and Hexadecyltrimethylammonium Bromide (HDTMA-Br) Surfactant-Modified Activated Carbon as Adsorbent for $Pb^{2+}$ and $NO_3$, *Jurnal Kimia Sains dan Aplikasi*, 23, 11, (2020), 396-402 https://doi.org/10.14710/jksa.23.11.396-402

[7] I. M. Onwuka, C. N. Madubuike, K. O. Chilakpu, Effectiveness of Coconut Shell Activated Carbon Filter Material Produced Under Various Carbonization and Activation Conditions, *International Journal of Advances in Scientific Research and Engineering (IJASRE)*, 4, 6, (2018), 68-75 https://doi.org/10.31695/IJASRE.2018.32752

[8] Hans Kristianto, Sintesis Karbon Aktif dengan Menggunakan Aktivasi Kimia $ZnCl_2$, *Jurnal Integrasi Proses*, 6, 3, (2017), 104-111 http://dx.doi.org/10.36055/jip.v6i3.1031

[9] Xuan Du, Wei Zhao, Shuhui Ma, Mingguo Ma, Tao Qi, Yi Wang, Chao Hua, Effect of $ZnCl_2$ impregnation concentration on the microstructure and electrical performance of ramie-based activated carbon hollow fiber, *Ionics*, 22, 4, (2016), 545-553 https://doi.org/10.1007/s11581-015-1571-3

[10] Heng Chen, Zaher Hashisho, Fast preparation of activated carbon from oil sands coke using microwave-assisted activation, *Fuel*, 95, (2012), 178-182 https://doi.org/10.1016/j.fuel.2011.10.045

[11] Abdurrahman Özhan, Ömer Şahin, Mehmet Maşuk Küçük, Cafer Saka, Preparation and characterization of activated carbon from pine cone by microwave-induced $ZnCl_2$ activation and its effects on the adsorption of methylene blue, *Cellulose*, 21, 4, (2014), 2457-2467 https://doi.org/10.1007/s10570-014-0299-y

[12] Milton J. Rosen, J.T. Kunjappu, Adsorption of surface-active agents at interfaces: the electrical double layer, in: *Surfactants and Interfacial Phenomena*, John Wiley & Sons, Inc., 2004, https://doi.org/10.1002/9781118228920.ch2

[13] U. O. Aroke, U. A. El-Nafaty, XRF, XRD and FTIR properties and characterization of HDTMA-Br surface modified organo-kaolinite clay, *International Journal of Emerging Technology and Advanced Engineering*, 4, 4, (2014), 817-825

[14] Akhmad Zainal Abidin, Tiara Puspasari, Hafis Pratama Rendra Graha, Utilization of Cassava Starch in Copolymerisation of Superabsorbent Polymer Composite (SAPC), *Journal of Engineering and Technological Sciences*, 46, 3, (2014), 286-298 http://dx.doi.org/10.5614/j.eng.technol.sci.2014.46.3.4

[15] Siriporn CHAEMSANIT, Narumol MATAN, Nirundorn MATAN, Activated carbon for food packaging application, *Walailak Journal of Science and Technology (WJST)*, 15, 4, (2018), 255-271 https://doi.org/10.48048/wjst.2018.4185

[16] Cafer Saka, BET, TG-DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with $ZnCl_2$, *Journal of Analytical and Applied Pyrolysis*, 95, (2012), 21-24 https://doi.org/10.1016/j.jaap.2011.12.020

[17] Marco Paini, Sean Ryan Daly, Bahar Aliakbarian, Ali Fathi, Elmira Arab Tehrany, Patrizia Perego, Fariba Dehghani, Peter Valtchev, An efficient liposome

based method for antioxidants encapsulation, *Colloids and Surfaces B: Biointerfaces*, 136, (2015), 1067–1072 https://doi.org/10.1016/j.colsurfb.2015.10.038

[18] Yingying Zhou, Zhenghua Wang, Andrew Hursthouse, Bozhi Ren, Gemini surfactant-modified activated carbon for remediation of hexavalent chromium from water, *Water*, 10, 1, (2018), 91 https://doi.org/10.3390/w10010091