



## Adsorption of sodium dodecylbenzene sulfonate (DBS) by c-3,4-di-methoxyphenylcalix [4]resorcinarene triphenylphosphonium chloride

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### ABSTRACT

Surfactants have been widely used in many industries, one of them is sodium dodecylbenzene sulfonate (DBS) which is a major component used in the manufacture of detergents and considered as toxic material. Various methods have been undertaken to reduce DBS content in water. One of them is adsorption, which is known as the most effective and environmentally friendly method so far. Our previous study has successfully synthesized an adsorbent C-3,4-dimethoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride (CRP). The aim of this study is to investigate the adsorption of DBS by CRP. Adsorption studies were carried out using the batch methods at different acidity, contact time, and initial DBS concentration and analyzed using UV-Visible, FTIR, and SEM-EDX spectrophotometer. The results showed the optimum condition of DBS adsorption was at pH 8, contact time 120 min, and DBS concentration 40 mg/L. The maximum capacity for the adsorption process was 12.93 mg/g. The rate of adsorption was found to follow the pseudo second-order kinetic model and the Langmuir adsorption isotherm. The mechanism was a chemisorption that occur in monolayer ( $\Delta G^\circ_{ads} = -24.87$  kJ/mol).

## 1. INTRODUCTION

Surfactants have been widely used in various industries such as paper, electroplating, cosmetics, food, pharmaceutical, and laundry industries. The classification of surfactants is divided into 3 types: cationic, non-ionic, and anionic. Anionic surfactants are produced about 60% compared to other species (Karray et. al., 2016). Sodium dodecyl benzene sulfonate (DBS) is the major component used in detergent manufacturing (Taffarel & Rubio, 2010). The disposal of surfactant directly into water can lead into serious environmental pollution and is relatively difficult to be degraded (Lechuga et. al., 2016; Jardak, 2016). The high

concentrations of DBS in the environment could be potentially xenobiotic compounds that are toxic. DBS can affect the mobility of organic compounds and minerals present in the soil/sediment to enter into plants thus interfering with the process of photosynthesis in plant leaves (Edwards et. al., 1994). Acute toxicity of DBS has a value of LD<sub>50</sub> 400-5000 mg/kg body weight (OECD, 2005). DBS enter the fish body through its gills and skin (Ying, 2006) which can cause death (Budiawan et. al., 2009).

Various methods have been done to reduce surfactant concentration such as coagulation methods (Beltran-Heredia et al, 2009), photocatalytic oxidation (Ono et. al., 2012), precipitation (Takayanagi et. al., 2017),

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and adsorption (Wulandari et. al., 2016). Adsorption is one of the most effective and environmentally friendly method. Some of the adsorbents that have been used to reduce the DBS content are natural zeolite-CTAB (Taffarel & Rubio, 2010), activated carbon (Zhao et. al., 2013), and C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene triphenyl-phosphonium chloride (CERP). Adsorption of DBS using CERP is optimal at pH 8, contact time 120 min, and DBS concentration of 40 mg/L. The adsorption follows the second order pseudo and the Langmuir adsorption isotherm through chemisorption with  $\Delta G = -23.83$  kJ/mol and a maximum adsorption capacity of 11.53 mg/g (Wulandari & Jumina, 2016).

The usage of calix [4] resorcinene compound as a DBS adsorbent is still limited thus still needs to be developed. This effort has been made by synthesizing C-3,4-dimethoxyphenylcalix [4] resorcinarene triphenyl-phosphonium chloride (CRP). CRP is synthesized from vanillin through methylation reaction, electrophilic substitution of aromatic-cyclization, chloromethylation and nucleophilic substitution which has 97.14% yield with a melting point of 296 °C (Wulandari & Jumina, 2016). The ability of CRP in adsorbing Cr (VI) has been studied and it is known that its maximum adsorption capacity of Cr (VI) is 15.71 mg/g which occurs by chemisorption ( $\Delta G = -36.24$  kJ/mol) (Wulandari & Jumina 2016) however the ability of CRP in adsorbing DBS has not been studied yet. In this study, the ability of CRP to adsorb DBS was studied based on the influence of pH, contact time, and DBS concentration.

## 2. METHODS

### 2.1 Material and Equipment

Materials used in this study were methylene blue (MB) reagent 100 mg/L, Whatman 42 filter paper, H<sub>2</sub>SO<sub>4</sub> 6N, sodium phosphate monohydrate (NaH<sub>2</sub>PO<sub>4</sub>:H<sub>2</sub>O), 100% DBS (w/v), CRP, distilled water, and chemical reagents used in sample analysis. All chemicals used were analytical grade and CRP used in this research was synthesized from previous research. CRP was synthesized

through methylation reactions, electrophilic substitution, cyclization-condensation, chloromethylation, and aromatic nucleophilic substitution (Wulandari & Jumina, 2016). The equipment used in this study were laboratory glassware, analytical scales, magnetic stirrer, pH meter, UV-Visible spectrophotometer (Shimadzu, UV-1800), Fourier Transform Infrared Spectroscopy (Shimadzu, Prestige 21) in the range of 4000-400 cm<sup>-1</sup> wave numbers, and Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX) (JEOL JD-2300) measured at a voltage of 15 keV with 10000 times magnification.

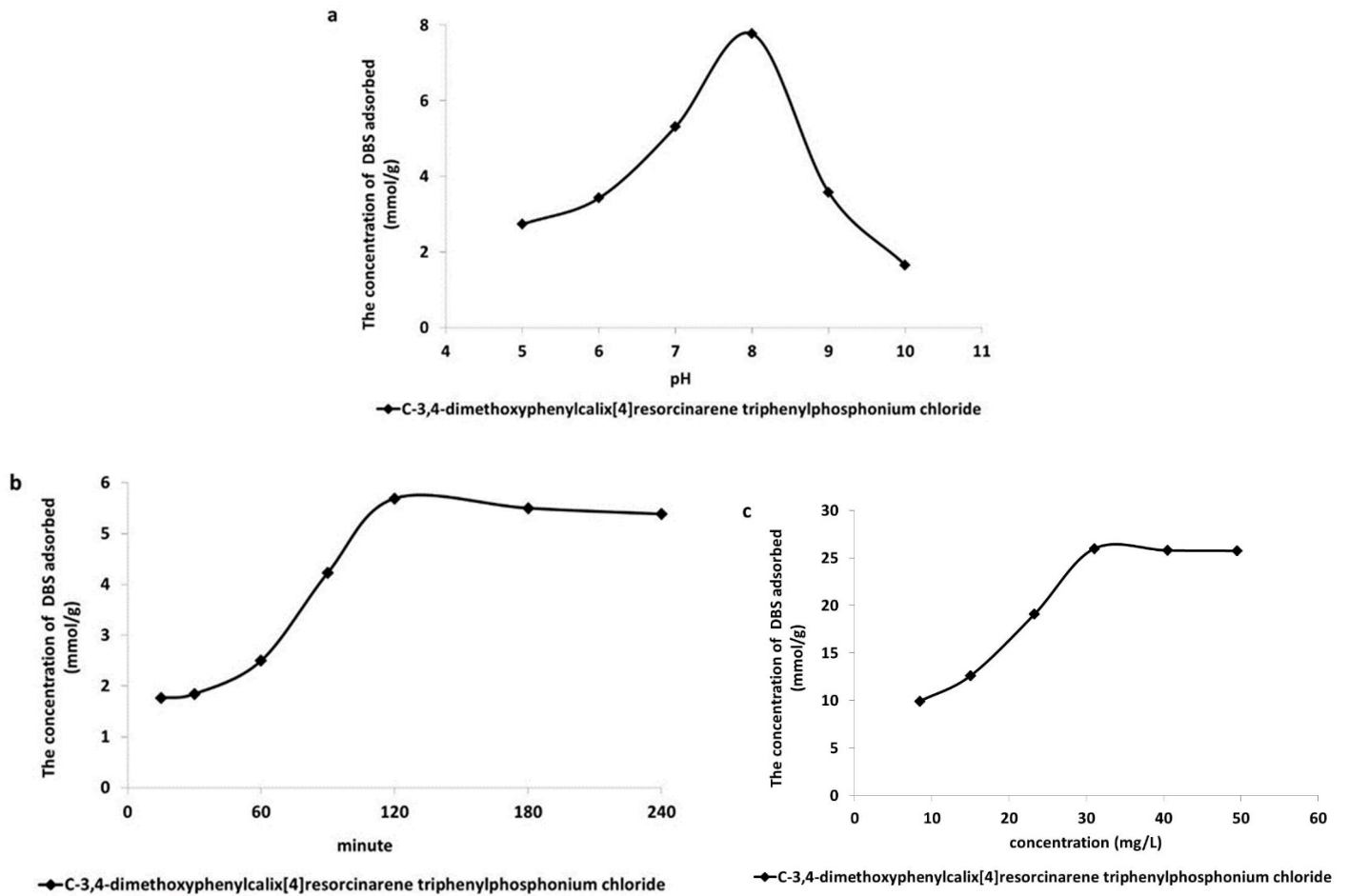
### 2.2 Procedure

The adsorption study was conducted through batch method and adsorption parameter such as acidity, contact time, and DBS concentration were determined as research parameter. The effect of acidity was observed in pH range 5-10, contact time 15; 30; 60; 90; 120; 180; and 240 min, and the effect of DBS concentration was observed at concentrations of 10, 20, 30, 40, 50, and 60 mg/L. Adsorption was performed by adding 0.002 g of CRP into 100 mL of DBS solution. The solution was stirred for 3 hours at 25 °C, then centrifuged for 20 minutes at 3500 rpm. The centrifugation result was filtered with Whatmann 42 filter paper then the filtrate was added with 25 mL MB complexing solution and 10 mL chloroform then extracted. The obtained organic phase was analyzed using UV-Visible spectrophotometer at 625 nm wavelength. The standard curve was made from a series of DBS standard solutions with concentrations 0.1; 0.2; 0.4; 0.6; 0.5; 1; 2; 3; and 4 mg/L. The adsorbed DBS surfactant concentration was obtained from the initial concentration of DBS surfactant reduced by the residual DBS surfactant concentration. The concentration of DBS that absorbed into the CRP compound was calculated based on the difference between the initial concentration ( $C_0$ ) and the residual concentration in the solution at time t ( $C_t$ ). The experiment was performed with 3 repetitions (triplo). The interaction of CRP with DBS then studied through spectroscopic analysis with FTIR and SEM-EDX.

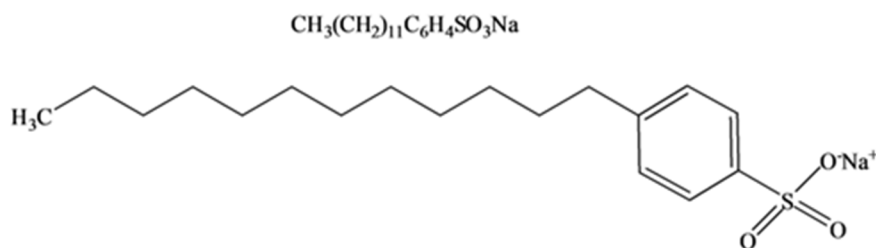
### 3. RESULT AND DISCUSSION

The effect of acidity on DBS adsorption by CRP showed that adsorption occurred optimally at pH 8. Under

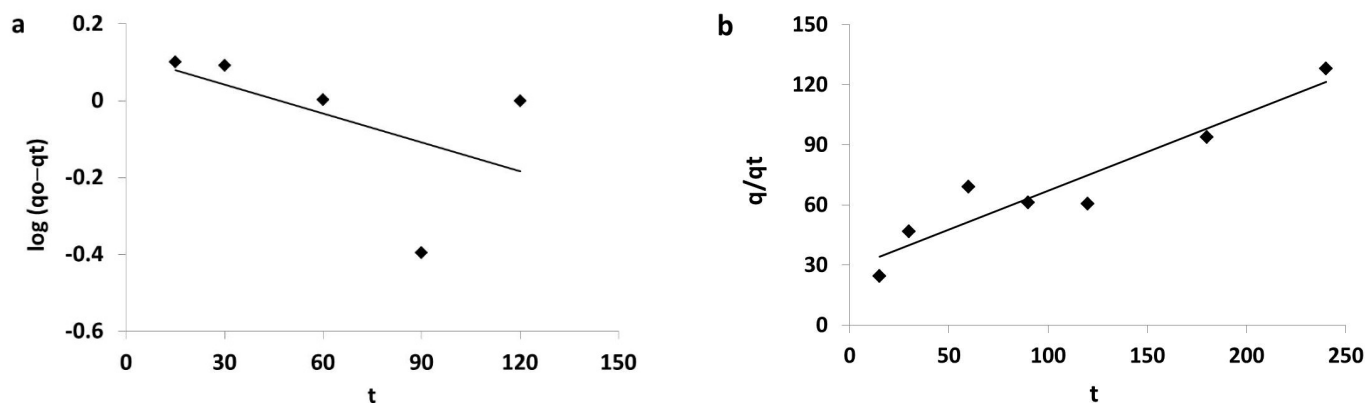
basic condition, DBS tended to be in its anion form (Fig. 1).



**Figure 1.** Effect of pH (a), contact time (b), and concentration (c) in DBS adsorption by CRP



**Figure 2.** DBS in its anion shape (Manousaki et. al., 2004)



**Figure 3.** The pseudo first-order (a) and pseudo second-order (b) of adsorption kinetics in DBS adsorption by CRP

**Table 1.** Parameter value of DBS adsorption kinetics

MKinetics Model	Equation	$k \times 10^{-3}$ (g mmol <sup>-1</sup> minute <sup>-1</sup> )	R
Lagergren	$\log(1,3116 - q_t) = -0,0025 t + 0,1178$	2,5	0,2768
Ho dan McKay	$\frac{t}{q_t} = 0,3872 t + 28,3450$	5,29	0,8943

Based on the adsorption pattern at various contact times, it was shown that the ability of CRP in adsorbing the DBS anion increased significantly in the time span of 15–120 minutes and the adsorption equilibrium was reached at 120 minutes contact time. Observations through variation of DBS concentration on CRP adsorption power were performed to determine the maximum adsorption capacity of adsorbent to DBS anion. The optimum concentration of DBS adsorption by CRP was 40 mg/L. The decreased of DBS adsorption at contact time above 120 minutes and at concentrations above 40 mg/L due to saturation of the active site of CRP which has quarterner phosphonium group that positively charged.

The pattern of DBS adsorption by CRP was based on time changing the studied according to pseudo first-order of Lagergren adsorption kinetics model (Ho, 2004) and pseudo second-order Ho and McKay (2000).

Based on adsorption kinetics result, it tends to follow the Ho and McKay pseudo second-order of adsorption kinetics model with linearity level closed to 1 and adsorption rate constant was  $5,29 \times 10^{-3}$  g mmol<sup>-1</sup> minutes<sup>-1</sup>. DBS adsorption by CRP then studied using

Langmuir isotherm model ( $\frac{1}{q_e} = \frac{1}{(X_m \cdot K \cdot C_e)} + \frac{1}{X_m}$ ) and Freundlich ( $\log q_e = \log K + \frac{1}{n} \log C_e$ ).

Based on Figure 4, the DBS adsorption occurred in this study followed the Langmuir isotherm adsorption model equation. The maximum adsorption capacity and the adsorption energy of DBS on CRP were summarized in Table 2.

The calculation of adsorption energy on CRP was determined by Gibbs free energy equation ( $\Delta G^\circ_{\text{ads}} = -RT \ln K$ ). The adsorption energy obtained for  $-24.87$  kJ/mol was classified as chemical adsorption (Adamson, 2004). The chemical adsorption from interaction between the DBS anion and CRP was caused by the presence of an active site of quarternary phosphonium groups that could interact with the DBS anion. DBS anion adsorption by CRP only occurred under basic condition. The interaction mechanism in CRP with DBS anion should be preceded by DBS protonation. The proposed interaction model of CRP with DBS anion was shown in Figure 5.

Confirmation of the interaction between CRP and DBS anion as a target for trapping was done through spectroscopic studies using IR and SEM–EDX spectrometry

method. Based on the IR spectra from the CRP–DBS and CRP complexes that had not interacted with DBS anion, there were a significant differences of absorption in certain wave number (Figure 6). Reduced absorption intensity at wave numbers 748  $\text{cm}^{-1}$  and 694  $\text{cm}^{-1}$  and absorption loss at

493  $\text{cm}^{-1}$  wave numbers in the IR spectrum (Fig. 6b) indicated that the quarterner phosphonium had interacted with DBS anion and left the hydroxy group which was still readable on 3425  $\text{cm}^{-1}$ . Thus, the CRP–DBS complex has been formed.

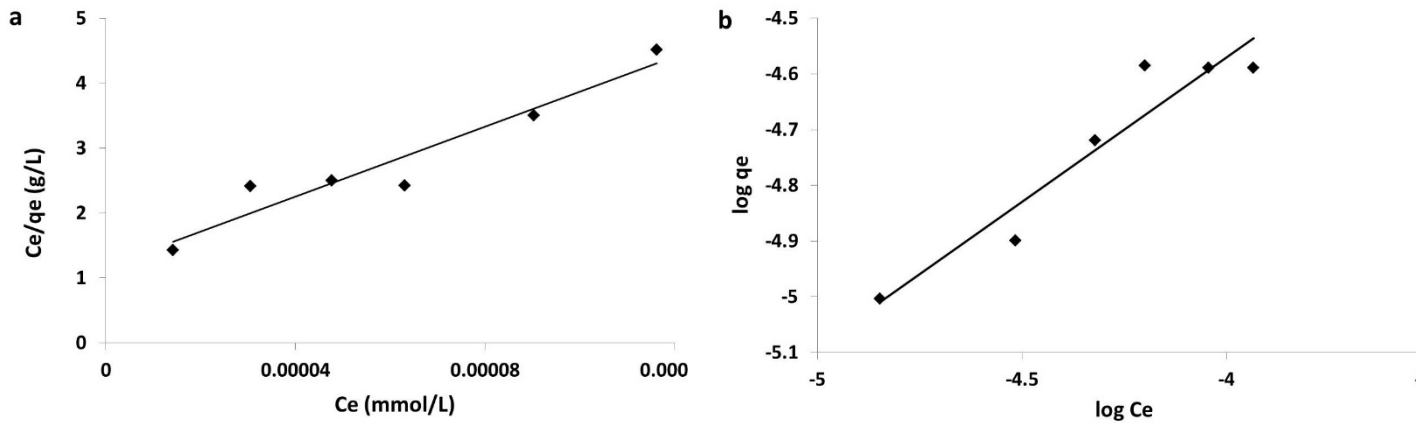


Figure 4. Langmuir (a) dan Freundlich (b) isotherm adsorption

Table 2. Capacity and energy of DBS adsorption by CRP

Isoterm Adsorption Model	Slope ( $1/X_m$ )	$q_m$ (mg/g)	intercept $1/(X_m \cdot K)$	$K$ (L/mol)	$\Delta G^\circ \text{ Ads}$ (kJ/mol)
Langmuir	26948	12.93	1.1738	22957.91	-24.87

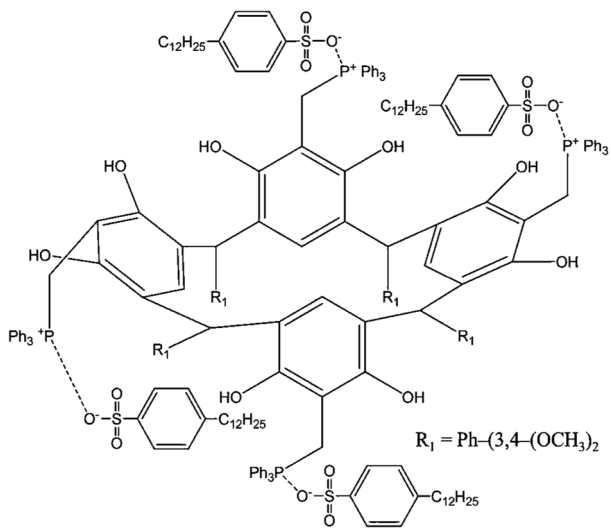


Figure 5. The adsorption interaction model of DBS by CRP (Utomo, 2012)

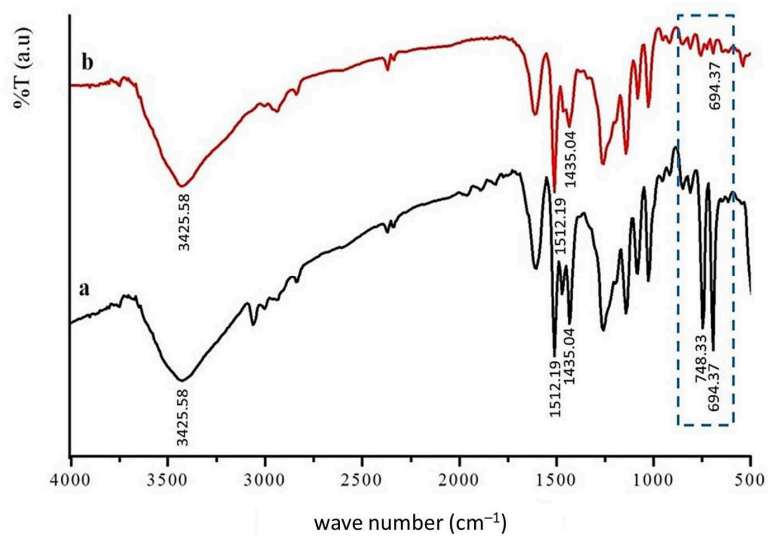


Figure 6. The FTIR spectra of CRP (a) and CRP–DBS complex (b)

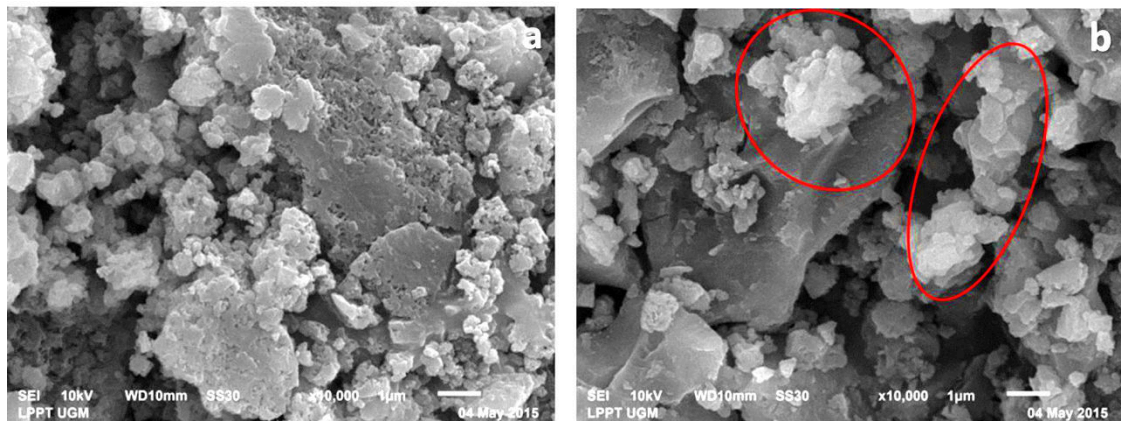


Figure 7. SEM of CRP (a) and CRP-DBS complex (b)

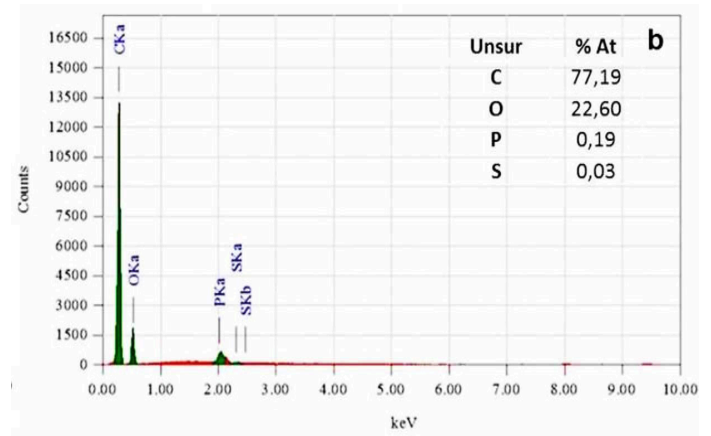
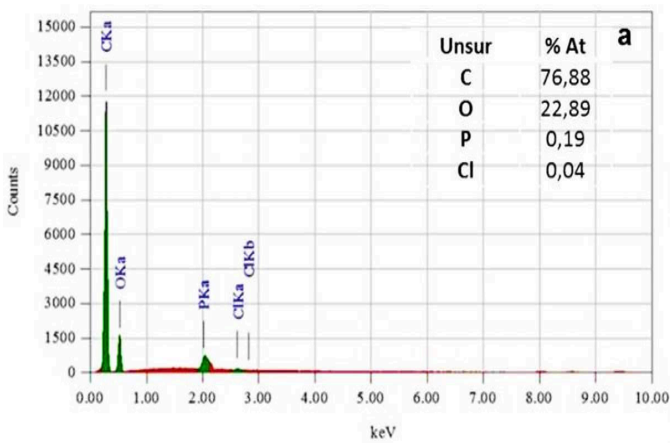


Figure 8. EDX of CRP (a) and CRP-DBS complex (b)

Characteristics of microstructure, energy, and percentage of chemical constituents in both CRP and CRP-DBS complexes were determined using SEM-EDX under operating conditions at a voltage of 15 keV and 10,000x magnification. Through enlarging 10,000x in SEM image (Fig. 7), it was clear that there were differences in the appearance of microstructure of CRP before and after adsorbing DBS anion. In the CRP-DBS complex SEM image, it appeared that the CRP surface has been covered by the DBS anion. This indicated that the CRP-DBS complex has been formed.

The formation of the CRP-DBS complex was further proved by elemental analysis to determine the

content of elements and compounds in the complex through quantitative analysis of EDX. Through EDX it would be known that the element content in both CRP and CRP-DBS complex to SEM image of 10,000x magnification (Fig. 8). The elemental scanning results showed some of the dominant elements C, O, and P as well as the little Cl elements present in CRP. An important finding of SEM-EDX analysis was the replacement of Cl elements on CRP by S elements of DBS with 0.07% mass percentage. This showed that there was an interaction between CRP and DBS anion. The interaction that occurred indicated that the CRP-DBS complex has formed.

## CONCLUSION

Based on the adsorption study, it can be concluded that the adsorption of DBS by CRP in forming CRP-DBS complex was effective at optimum condition pH 8, contact time 120 min, and DBS concentration 40 mg/L. The adsorption followed a pseudo second-order kinetic model and the Langmuir isotherm adsorption which proceeded in a monolayer with a maximum adsorption capacity of 12.93 mg/g.

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