Adsorption and Desorption Carotenoids of Raw Palm Oil (Crude Palm Oil/CPO) using Salt M-Polystyrene Sulfonate (M = Na, Mg, Ca, Sr and Ba)

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Abstract

Adsorption and desorption of carotenoids from crude palm oil (CPO) has been performed in ethanol, using five types of adsorbents M-Polystyrene Sulfonate or M-PSS (M = Na, Mg, Ca, Sr, and Ba) which is Sulfonate salts. NaPSS first adsorbents is made by neutralizing a solution of polystyrene sulfonic acid with acetyl sulfate. Four other M-PSS adsorbents are made from a reaction between Na-PSS with each salt MgCl₂, CaCl₂, SrCl₂ and BaCl₂. The five adsorbents are characterized by Melting Point Apparatus (MPA), Spectrophotometry Atomic Absorption (SAA), Transform Infra Red Spectrometer (TIRS), Scanning Electron Microscope (SEM), Surface Area Analyzer with Brunauer Emmet Teller (BET) and Transmission Electron Microscope (TEM). The treatment resulted in the adsorption 100%, desorption 78.75% and the carotenoids recovered 78.75%.

Keywords: CPO, Carotenoids, Polystyrene Sulfonate, Adsorption, Desorption, Recovery

1. Introduction

Indonesia is the most producer of palm oil (Crude Palm Oil/CPO) in the world with palm oil production of 25.4 million metric tons a 2012. Indonesian CPO majority (65%) are still largely exported as raw material, the rest (35%) is used for domestic needs as raw material for cooking oil, margarine, shortening and a small portion is used as a raw material for biodiesel and oleochemicals including fatty acids, fatty alcohol and glycerine.1

CPO is a source of natural carotenoids, constituting about 500–700 ppm². So it can be used as a source of provitamin A and antioxidant²⁻³ Carotenoids is not only needed for food industry, and pharmaceutical, but also for cosmetic industries³. In the food industry it is used nutritional and coloring ingredients, in the pharmaceutical industry it is used as an ingredient of medicines and while in the cosmetics industry it is used as a beauty ingredient²⁻³

In the process of making cooking oil using palm oil as a source of raw materials, this carotenoids are wasted in vain⁴, because carotenoids adsorbed on the bleaching process can no longer be recovered⁵. The same thing also occurs in the process of making oleochemical, because carotenoids damaged by the use of high temperature and pressure. Therefore, it is necessary to find an attempt to recover the temporary CPO carotenoids can still be used as an oil feedstock and oleochemicals⁶. Various attempts to obtain compounds carotenoids are attempted continuously by various methods, one of them is the method of adsorption⁷.

Lately carotenoids separation of CPO has been done by using adsorbents, without reducing the quality of the CPO to be used as raw materials of other products⁸. In the adsorption process adsorbent carotenoids has interaction between the molecular adsorbents with carotenoids. There are two types of adsorbents natural and synthetic.
adsorbents. Natural adsorbents are activated carbon, bleaching earth, rice husk ash, starch, montmorillonite clay, while the synthetic adsorbents polymer are polystyrene sulfonate (PSS), copolymer divinyl benzene styrene, Diaion HP series (Diaion HP 10–50) and SP series (SP 800–875, SP 205, SP 207). Yet from all reports, although these adsorbents has had a high adsorption power, between 17–100%, and the recovery is still low rate between 40–65%.

One of the efforts is to increase the rate of adsorption carotenoids of CPO and simultaneously increase the recovery rate carotenoids is to synthesize an adsorbents which also contains a cluster of nonpolar and polar groups. So that the interaction between the nonpolar groups carotenoids chains and metal-containing polar groups interact with the double bond of carotenoids. In this case, rich double bond electrons carotenoids interact with the empty d orbitals of the metal, while the nonpolar hydrocarbon chain carotenoids interact with the Van der Walls force. Based on these, there is an idea to create a group-containing polymer adsorbents nonpolar (hydrocarbons) and polar group metals M (M = Na, Mg, Ca, Sr, and Ba). The form of bonding that occurred allegedly as in Figure 1.

In pictorial polymers derived from styrene divinyl benzene sulfonate M-polystyrene sulfonate salt (M-PSS) as an adsorbents to form bonding interactions that occur with compounds carotenoids depicted as Figure 2.

This paper reported five (5) types of adsorbents, namely Na-, Mg-, Ca-, Sr- and Ba-PSS were used to adsorb carotenoids on CPO and reviewing carotenoids desorption rate of each adsorbents.

2. Materials and Method

2.1 Materials and Equipments

The material used is Polystyrene (PS) pa, BM: 192,000 from Aldrich Chemistry, American products were obtained from Sigma Chemie GmbH, CPO containing 479.7 ppm β-carotene derived from palm oil mill (POM) Merbau Fence Limited PTPN II Tanjung Morawa Field Indonesia, Acetic anhydride, Chloroform, H2SO4 (p), MgCl2.6H2O, CaCl2.2H2O, SrCl2.6H2O, BaCl2.2H2O and ethanol solvents, n-hexane pa standards obtained from Merck and used as such, Nitrogen gas (N2) from PT. Aneka Gas Field while β-carotene standard was obtained from Sigma-PT Jakarta.

The equipment used is a vacuum rotary evaporator, AAS (Atomic Absorption Spectrophotometry) of type AA7000 Shimadzu, FT-IR (Fourier Transform-Infra Red) of type Shimadzu 8400S, SEM (Scanning Electron Mikroscopy) Brand Zeiss Evo 10, Gallenkamp Melting Point Apparatus type the maximum temperature of 350°C, the BET (Brunauer Emmett Teller), TEM (Transmission Electron Microscopy) type JEOL/EO JEM-1400, Shimadzu GC-MS of type 2010 with Restek-5MS column, UV-visible spectrophotometer from spectronic type 20 Milton Roy.

2.2 Experimental

2.2.1 Making of Polystyrene Sulfonate

Polystyrene sulfonate is made of 3 parts, namely the manufacture of acetyl sulfate, solution preparation polystyrene...
and polystyrene sulfonation with acetyl sulfate.\textsuperscript{11,12} First manufacture of acetyl sulfate, was added to a three neck flask 10 ml of chloroform. Add 10 ml of acetic anhydride (acetic anhydride performed for pipette place that is not exposed to sunlight and covered with a napkin as acetic anhydride easily hydrolyzed to 2 moles of acetic acid). Then add H.<sub>2</sub>SO<sub>4</sub> (p) through the funnel 10 ml dropper, distirer, flashed with sufficient N<sub>2</sub> for 1 hour in an ice bath (\(< 0 \, ^\circ\text{C}\)) was continued for 1 hour at room temperature. Both the manufacture of polystyrene solution, incorporated into a two neck flask 10 g of polystyrene pa, diluted with 70 ml of chloroform and then flashed with N<sub>2</sub>, distirer then heated to dissolve polystyrene at a temperature of 40–45\(^\circ\text{C}\). Then the third sulfonation of polystyrene with acetyl sulfate.

Dropper funnel inserted into the reaction product of acetyl sulfate, dripped slowly into a flask containing a solution of polystyrene and then flashed with N<sub>2</sub> and then heated at a temperature of 40–45\(^\circ\text{C}\) for 2 hours while distirer. The results computed by 9.1% sulfonation degrees and characterized obtained by FT-IR SO: 1124.40 cm\(^{-1}\).

\section*{2.2.2 Making of Adsorbent M-PSS Salt}

There are five (5) types of adsorbents were synthesized as follows: First Sodium polystyrene sulfonate (Na-PSS) was prepared by neutralizing a solution of 51 g of solid polystyrene sulfonic acid in 250 ml of distilled water with acetyl sulfate in 110 ml of 10% methanolic NaOH. Ethanol is added to the solution resulting in a white precipitate was then filtered and the precipitate was dried in vacuum, then the solids obtained were weighed and counted yielding. While the 4 (four) different adsorbents namely Mg-, Ca-, Sr- and Ba-PSS prepared by reacting Na-PSS with each salt MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub>, BaCl<sub>2</sub> in water.

For details of making MgPSS following into a 250 ml glass beaker, suspended 4 g Na-PSS in 20 ml of water and add 50 ml of 10% MgCl<sub>2</sub> solution, stirred for 7 hours. The result of this reaction was filtered, the solid washed with ethanol and dried in vacuum. Similarly followed for Ca-, Sr-, and BaPSS. Then the solids obtained from the five adsorbents were weighed, analyzed the metal content by SAA, melting point (MP), further characterized by FT-IR, SEM, BET and TEM test. For Ca-PSS adsorbents made 100 and 150 mesh sizes, CaPSS crushed in a mortar, then sieved using a screen and 150 mesh.

\section*{2.2.3 Adsorption and Desorption Carotenoids of CP}

It is inserted 3 g CPO carotenoids containing 479.70 ppm into a 20 ml test tube dissolved in ethanol and 15 ml (1.44 mg carotenoids amount), was added 0.75 g of Ca-PSS. The mixture was centrifuged and then filtered. The filtrate was tested levels of UV-Vis carotenoids with.\textsuperscript{13} Then carotenoids adsorbed on the adsorbents using n-hexane desorption. The filtrate was concentrated to obtain concentrate carotenoids to know the level of desorption and recovery.

In the same way the adsorption process carotenoids of CPO was conducted for adsorbents Na-, Mg-, Sr and Ba-PSS. Further, adsorption of carotenoids is done by varying the amount of adsorbents CaPSS namely 0.25, 0.50, 0.75, 1.0, 1.25 and 1.50 g. To see the effect of the concentration in the solution carotenoids CPO conducted in the same manner as procedure 2.2.3, for adsorption carotenoids. The concentration in CPO with various carotenoids namely: 0.48; 1.44; 2.40; 3.36 and 4.32 mg using 1.0 gr of Ca-PSS 100 mesh. Meanwhile, to see the effect of particle size of the adsorbents is done in the same manner as procedure 2.2.3. 1.0 gr adsorbents for Ca-PSS for particle sizes of 100 and 150 mesh.

\section*{3. Results and Discussions}

\subsection*{3.1 Making of Adsorbent}

In this study, there are five (5) types of adsorbents polystyrene sulfonate salt (M-PSS) which synthesized. First Na-PSS was made by neutralizing a solution of polystyrene sulfonic acid with NaOH solution, while the 4 (four) types again that Mg-, Ca-, Sr- and Ba-PSS prepared by reacting Na-PSS with magnesium chloride, calcium chloride, strontium chloride and barium chloride in water. From the results obtained adsorbents synthesis reaction NaPSS yield as much as 57 grams with 88.42%, while as many as 3,871 g MgPSS, CaPSS: 4.026 g, SrPSS: 3.57 g and BaPSS: 4.05 gr. Melting point measurements (MP) of the five adsorbents M-PSS is >350\(^\circ\text{C}\) because at this temperature the adsorbents material decomposition yet, still stable and no decomposition of the polymer showed good stability at high temperatures.

The test results of the five adsorbents gave spectroscopy FTIR spectra of Na-PSS which gives SO: 1189.1 cm\(^{-1}\), MgPSS, SO: 1168.0 cm\(^{-1}\), CaPSS, SO: 1170.0 cm\(^{-1}\), SO:
1170.0 cm\(^{-1}\), SrPSS SO\(_3\): 1178.1 cm\(^{-1}\) and BaPSS, SO\(_3\): 1183.0 cm\(^{-1}\). The results of FT-IR spectra can be seen in Figure 3.

Figure 3 shows that the FTIR spectra indicate that there is a shift in the SO vibration which occurs NaPSS new compounds, MgPSS, CaPSS, SrPSS and BaPSS. The existence of the cluster [-SO_3-] in which the adsorbents SO\(_3\): 1195–1168 cm\(^{-1}\).\(^{14}\)

Morphology character of the five adsorbents are done by SEM photo with magnification 20 µm size and the result can be seen in figure 4.

In Figure 4, the data magnification SEM image with 20 µm, is clearly visible material particles are almost spherical shape (spherical) with uniform size (uniform). Then there is a change of particles dispersed in a free state and there is also a form aggregates\(^{15}\).

From Figure 5, with magnification TEM image data visible 200 nm MPSS adsorbents material. TEM of the fifth Test Results adsorbent can be seen in Figure 5 has spherical particles (spherical) are dispersed and there is no inter-forming aggregates, and skin (a shell) on the outer dark\(^{15}\).

From the test results of the five adsorbents BET salts M-PSS has a rather closed pores which have a value of 0.001 m\(^2\)/gr area. This is consistent with the nature of the M-PSS salt that has properties of gel type resins\(^{16}\).

The results of the test assay with AAS, of the five M-PSS salt adsorbents, respectively Na metal content: 775.42 ppm (33.71 mmol), metal content Mg: 397.53 ppm (16.56 mmol), the metal content of Ca: 661.16 ppm (16.53 mmol), metal content Sr: 1252.4 ppm (14.30 mmol) Ba and metal content: 2013.5 ppm (14.69 mmol).

![Figure 3. FT-IR NaPSS, MgPSS And CaPSS spectrum.](image1)

![Figure 4. Photo SEM Material Adsorbent MPSS with magnification 20 µm.](image2)

![Figure 5. Photo TEM Material Adsorbent M-PSS with Magnification 200 nm.](image3)
Results characterization of five M-PSS salt adsorbents obtained for the metal content, melting point (MP), SO_2 (FTIR), the pores (BET), SEM test and TEM test can be seen in Table 1.

Table 1 shows that there has been a change of metallic Na by Mg, Ca, Sr, and Ba Na metal which is replaced by Mg of 98.25%, 98.07% Ca: Sr: Ba 84.84% and by as much as 87, 21%, this suggests that magnesium, calcium, strontium and barium salts PSS formed at which the reaction occurs between Na-PSS with M-chloride salt (M: Mg, Ca, Sr, and Ba).

### 3.2 Adsorption and Desorption Carotenoids from CPO by M-PSS (M = Na, Mg, Ca, Sr dan Ba)

To know the level of adsorption, carotenoids and recovery rate the CPO of the five types of adsorbents, adsorption is carried out at a carotenoids concentration of 1.44 mg carotenoids (3 g CPO) in 15 ml of ethanol using CPO in Na-PSS, PSS-Mg, Ca PSS-, Sr-and Ba-PSS PSS as much as 0.75 g with a particle size of 100 mesh and desorption of the adsorbents which has carotenoids containing carotenoids by dissolving n-hexane and the results can be seen in Figure 6.

From Figure 6, it is seen that although the adsorbents Mg-, Sr-, and Ba-PSS give a higher adsorption rate than the Ca-PSS, but it gives a lower desorption, it is because the Mg-, Sr-and Ba-PSS can only Substituting Na metal at 98.25; 84.84; 87.21% and 98.07% Ca-PSS. Thus only a portion of Mg metal that can interact with the double bond carotenoids. This is thought to be caused by interaction between the double bond in carotenoids with metal d orbitals on Ca weaker than the same interactions with metals Mg, Sr, and Ba so that the Ca-PSS carotenoids more detached than that released by metal Mg, Sr and Ba.

### Table 1. The character from the five adsorbents M-PSS

| NO | Adsorbent type | The solid obtained, gr | Metal content, mmol/kg | \( \nu_{so}, \text{cm}^{-1} \) | Melting point, °C | Pores(BET) | SEM | TEM |
|----|----------------|------------------------|------------------------|----------------------------|------------------|------------|-----|-----|
| 1  | Na-PSS         | 57                     | 33.71                  | 1189.1                     | >350             | Rather closed (small pores) | figure 4 | figure 5 |
| 2  | Mg-PSS         | 3871                   | 33.71                  | 1189.1                     | >350             | Rather closed (small pores) | figure 4 | figure 5 |
| 3  | Ca-PSS         | 4026                   | 16.53                  | 1168.0                     | >350             | Rather closed (small pores) | figure 4 | figure 5 |
| 4  | Sr-PSS         | 3570                   | 14.30                  | 1170.0                     | >350             | Rather closed (small pores) | figure 4 | figure 5 |
| 5  | Ba-PSS         | 4050                   | 14.70                  | 1183.0                     | >350             | Rather closed (small pores) | figure 4 | figure 5 |
This can be seen in Figure 1 and 2, which show that the interaction between the adsorbents carotenoids do not involve pore because the test results according to the BET pore is very small (closed pore) and therefore adsorption is functioning in a non-polar interactions with non-polar and metal interaction with the double bond carotenoids. Regarding the level of desorption, Ca-PSS adsorbents is much larger than the Na-, Mg-, Sr-, and Ba-PSS, then the next thing studied only for the level of adsorption and desorption of adsorbents Ca-PSS, especially the influence of the amount of adsorbents, particle size the concentration of adsorbents and carotenoids on CPO solution in ethanol.

### 3.2.1 Influence of Amount of Adsorbent

To know the level of adsorption, desorption and recovery of Ca-PSS based on the amount of adsorbents, the adsorption carotenoids done by varying the amount of adsorbents of 0.25, 0.5, 0.75, 1.0, 1.25, and 1.5 g for the concentration adsorb carotenoids with 1.44 mg of carotenoids in 15 ml of ethanol and palm oil in carotenoids desorption of the adsorbents which has contains carotenoids, for more details, comparison of the adsorption rate, desorption rate and recovery rate of variation in the amount of adsorbents can be seen in Figure 7.

Figure 7 reveals that the absorption rate increased with increasing amount of adsorbents until a saturation point is the amount of 1.0 gram of adsorbents subsequent constant, giving the absorption rate of 100%. The same thing happens for the desorption rate which increased with increasing adsorbents amount and rate of absorption, it also occurs in the amount of 1.0 gram of adsorbents due to absorption carotenoids of CPO by Ca-PSS is influenced by the amount of adsorbents used.

This occurs because of the greater amount of adsorbents, the interaction between the adsorbents and the conjugated double bond of the greater carotenoids that causes increased adsorption rate carotenoids until the saturation point is 100% and so on constantly.

In the desorption process, there are two important things to increase the rate of desorption is the first interaction that occurs between the metal calcium in Ca-PSS with conjugated double bonds of carotenoids, and secondly the ability to bind Ca-PSS stronger carotenoids of the fatty acid ester due to hydrocarbon chain length of Ca-PSS where carotenoids has a longer hydrocarbon chain than the hydrocarbon chain fatty acid esters that carotenoids will be retained on the Ca-PSS compared with the mixed fatty acid esters.

Therefore, the desorption rate does not continue to increase with increasing amount of adsorbents Ca-PSS; but achieved until the saturation point. So this constant occurs in 1.0 gram of adsorbents amount and rate of adsorption of 100% which gives the desorption rate of 78.75%.

### 3.2.2 Influence of Concentration of Carotenoids in Solution CPO

To know the level of adsorption, desorption and recovery carotenoids, the carotenoids concentration on the CPO in solution is done by varying the adsorption carotenoids. The carotenoids concentration of 0.48 mg (1 g CPO), 1.44 mg (3 g CPO); 2.4 mg (5 g CPO), 3.36 mg (7 g CPO), and 4.32 mg (9 g CPO) carotenoids in 15 ml of ethanol and then desorption CPO carotenoids of adsorbents which contained carotenoids, for more details adsorption rate comparison and desorption rate of the sixth carotenoids the concentration variation in CPO solution can be seen in Figure 8.
From Figure 8 seen that the rate of adsorption and the highest desorption rate is 100% and 78.75% is achieved on condition the carotenoids concentration of 1.44 mg (3 g CPO) CPO in 15 ml solution in ethanol. This happens because the physical mixture with ethanol carotenoids on CPO form two layers. The top layer is a phase of ethanol and undercoat reddish solid phase consists of carotenoids the fatty acid esters. Esters of fatty acids and ethanol to form a larger interface (large solubility) compared carotenoids with ethanol so that the presence of the fatty acid esters of ethanol will be extracted into the ethanol and carotenoids content in the mixture increases. In this case the influence the carotenoids concentration of CPO in solution in ethanol affects the rate of adsorption and desorption carotenoids of CPO as more ethanol is used, the levels carotenoids adsorbed more and more.

In this case, ethanol as a solvent has a very important role in the adsorption process. More ethanol is used in the media the movement of molecules of fatty acid esters is enhanced. So that the diffusion of fatty acid esters of ethanol will rise to phase followed by a decrease in the content of fatty acid esters in carotenoids result in adsorption. A decrease in the content of fatty acid esters in carotenoids adsorption results showed that ethanol has been partially dissolving the fatty acid esters of CPO. So the rate of the adsorption process is increasing and then decreasing as the ratio of the number carotenoids CPO solution was saturated with ethanol so that the rate of adsorption and desorption occurs, namely a decrease in carotenoids the concentration of 1.44 mg in 15 ml of CPO in ethanol. It suggests that the use of ethanol influences on the adsorption of carotenoids of CPO as fatty acid esters soluble in ethanol.

### 3.2.3 Influence of Adsorbent Particle Size

To know the level of adsorption, desorption and recovery in CPO carotenoids by particle size of the adsorbents, the adsorption carotenoids made against CPO in ethanol solution using a variation of the particle size of 100 and 150 mesh. The adsorption rate comparisons, desorption and recovery of the adsorbents particle size variations can be seen in Figure 9.

Figure 9 shows that the effect of particle size of the adsorbents with the adsorption rate and desorption carotenoids influence. The comparison between the level of adsorption rate and desorption with the same particle size range gives great results that the adsorption rate from 77.22 to 100% with a desorption rate of 35.25 to 65, 28 for the particle size of 100 mesh and 150 mesh. This is because the smaller the particle size of the adsorbent, the greater the surface area of the particles, the more extensive contact between the adsorbent with carotenoids. So the greater the adsorbance, but the smaller the particle size of the adsorbent is getting stronger bonds between the molecules of the adsorbent with carotenoids resulting in lesser desorption.

### 4. Conclusion

M-amberlite and M-PSS have been synthesized as an adsorbent that is combined with Na and Group IIA metals (M = Na, Mg, Ca, Sr, and Ba). The interaction between the adsorbents carotenoids do not involve pore because the test results according to the BET pore is very small (closed pore) and therefore adsorption is functioning in a non-polar interactions with polar and non-bonded interactions carotenoids metal. Among the five adsorbents, calcium polystyrene sulfonate salts demonstrated desorption and recovery rate as 78.75% which is the best.

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