Synthesis of Sorbitan Oleate from Sorbitol as Iron Adsorbent and Comparative Capacity of Adsorption on Pectin

Muhammad Arif Darmawan¹, Agustino Zulys¹.ᵃ), Misri Gozan²

¹Department of Chemistry, Faculty of Mathematics and Sciences, Universitas Indonesia
²Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia

ᵃ) Corresponding Author: zulys@ui.ac.id

Abstract. Heavy metal pollutant such as iron species is harmful to the environment and the health of living things. The method used in heavy metal adsorption was adsorbent such as biosorbents and synthetic adsorbents. In this research, sorbitan oleate was used as an iron (III) adsorbent which aims to determine the adsorption capacity of iron(III) with sorbitan oleate and its ratio to pectin. The synthesis of sorbitan oleate was carried out in two stages: dehydration of sorbitol into sorbitan and esterification of sorbitan with oleic acid to form sorbitan oleate. The greater the synthesis time, the acid number of sorbitan oleate synthesis is smaller. Adsorption of iron (III) ions with sorbitan oleate and pectin was carried out at varied temperature (20 °, 30 °, 40 °, 50 ° Celsius), time (30-180 min), and pH (4, 5, 6, 8, 9). There was found an optimum condition for sorbitan oleate at 20 °C, 30 minutes, and pH 4; While for pectin at 20 °C, 90 min and pH 5. Adsorption isotherms iron(III) with sorbitan oleate and pectin both follow Freundlich adsorption isotherms with adsorption capacity of iron (III) with sorbitan oleate and pectin respectively are 1.193 and 0.8304. The interaction of iron (III) ions with sorbitan oleate has a stronger interaction than pectin.

Introduction

Environmental pollution of heavy metals becomes a serious problem as the heavy use of heavy metals in the industrial field [1]. Heavy metals are toxic substances and generally carcinogenic. As a marine pollutant, heavy metals at high concentration are very harmful to living things. One of the heavy metals that has an adverse effect when the excess amount is the ferrous metal. At high concentrations, iron can form radical iron species due to non-binding iron species with proteins that can cause cell damage to living things [2]. Therefore, the concentration of ferrous metal ions in the environment must be maintained so as not to overdo in the environment.

An effort to overcome the problem of heavy metal waste pollution is applying an adsorbent to adsorb heavy metal ions. Many researches have been done to find out and use different types of adsorbents which are effective in reducing the amount of heavy metals such as using activated charcoal, nanoparticles and other types of adsorbents [3].

Pectin is one of the most widely used adsorbents for heavy metal adsorbents. Pectin can be obtained through an extraction process from natural materials such as banana peel, apple and others [4].

Sorbitan Oleate is one of the organic compounds belonging to the sorbitan ester group and is the result of esterification of sorbitan and oleic acid. The use of sorbitan oleate itself is widely used as emulsifier or surfactant due to sorbitan oleate having hydrophilic (like water) and lipophilic (like lipid) groups [5]. However, there are currently no studies using sorbitan oleates as heavy metal ion adsorbents.
Therefore, in this research will be studied whether the sorbitan oleate can be used as metal adsorption of iron and the ratio of its adsorption capacity by using pectin.

Method
Sorbitan oleates compound were synthesized by two stages, that is dehydration of sorbitol and esterification of sorbitan with fatty acids. Sorbitol was dehydrated using concentrated sulfuric acid for 45 minutes at 120 °C to produce sorbitan. Sorbitan esterification with oleic acid at a temperature of 180 - 200 °C and the presence of alkali catalyst. Synthesis time varied at 2, 4, 6 and 8 hours. Sorbitan oleate of synthesized product was tested its acid value with acid-base titration. Sorbitan oleate synthesized and pectin are reacted with iron metal ions in the presence of variations of pH (4, 5, 6, 8, 9), temperature (20, 30, 40, 50 °C), and time (30; 60; 90; 120; 180 minute). To identify the rest of iron metal contents at optimum condition, FAAS instrumentation was . After the optimum conditions are known, sorbitan oleate and pectin are respectively reacted with variations in the concentration of iron metal ions (50, 100, 150, 200 and 250 ppm) to determine the type of adsorption isotherm. The interaction between iron metal ions with sorbitan oleate and pectin is done with FTIR.

Result and Discussions
The synthesis of sorbitan oleate was carried out in two stages: dehydration of sorbitol and esterification of sorbitan with oleic acid. The first stage was dehydration of sorbitol by using concentrated sulfuric acid as a catalyst. Sorbitol was reacted to remove a mole of water by heating and the presence of an acid catalyst for the dehydration process. Acids which was used in this process are non-oxidizing acids such as sulfuric acid, phosphoric acid, hydrochloric acid or aryl sulphonic acids (such as p-toluene sulfonic acid). In this study we used sulfuric acid easily to obtain and a hygroscopic acid. The dehydration process was carried out for 45 minutes due to the conversion of sorbitan into isosorbide at higher temperatures which is the final stage product of the sorbitol dehydration process. The research conducted by Yabushita et al produced the time data to obtain optimum levels of the sorbitol dehydration process is a reaction of 45 minutes [6]. When the reaction time gets longer, it will decrease the sorbitan content formed due to change to isosorbide. Figure 1 is a reaction scheme of sorbitol dehydration.

![Figure 1. Sorbitol Dehydration Reaction](image)

Sorbitan synthesis then conducted esterification reaction with oleic acid and added NaOH to neutralize excess acid in dehydration sorbitol process. The reaction was carried out with the reflux system during the time variation of 2, 4, 6 and 8 hours. Sorbitan oleate synthesis then taken some parts and done the titration to measure the value of acid numbers. The acid number is the number of free fatty acids (oleic acid) that do not react with sorbitan to form sorbitan oleate. The lower the acid number, the less oleic acid because it has formed to form sorbitan oleate. Figure 2 shows the value of the acid number of sorbitan oleic synthesis. The greater the synthesis time, the acid number will be smaller because more oleic acid reacts with sorbitan to form sorbitan oleate. The acid value obtained in the study with synthesis time 2, 4, 6 and 8 hours were 147.26; 72.93; 50.49 and 24.289 mg KOH / g samples.
Sorbitan oleate that has been synthesized for 8 hours then reacted with iron ion solution to know the adsorption interaction that occurred and pectin as comparison. Some parameter variations were performed to determine the optimum conditions of the reaction, temperature variations (20 °, 30 °, 40 ° and 50 ° C.), time (30, 60, 90, 120, 150, and 180 min) and pH (4, 5, 6, 8 and 9). Figures 3 and 4 represent the optimization graph of iron ion interaction time with sorbitan oleate and pectin. Where Q value is the unit of adsorption efficiency used with units of mg of metal / gram adsorbent (sorbitan oleate or pectin) (mg / g).

In the research using sorbitan oleate, the optimum adsorption time of iron was 30 minutes with adsorption efficiency of 4.5 mg / g. While using pectin obtained optimum time for 90 minutes with adsorption efficiency of 3.76 mg / g. The difference phenomena is probably due to differences from the active site found in sorbitan oleate and pectin that serves as a place of interaction. In the sorbitan oleate, the amount of adsorbate (in this case the iron (III) ion) had reached equilibrium to interact with the oleic sorbitan at 30 minutes so as not to bind more iron (III) ions. Meanwhile, pectin adsorption took a longer time as 90 minutes to reach equilibrium, possibly because pectin is a polymer so many sites to bind iron (III) ions.
Figures 5 and 6 show temperature variations of iron ion (III) reactions with sorbitan oleate and pectin. Based on the graph data from temperature variation of iron adsorption (III) with sorbitan oleate and pectin there is a similarity of phenomenon, that is decreasing adsorption with increasing temperature. The increased temperature causes the energy and ion reactivity to increase so that more ions are able to pass energy levels to interact with sites on the surface. The greater ionic reactivity will also increase ion diffusion in the pores of the adsorbent. However, an increase in temperature that causes increased ionic reactivity will interfere with the interaction that has been formed. The optimum temperature obtained from both adsorption was 20 °C.

In Figure 7, it is known that the greater pH value in the adsorption process using sorbitan oleate, the smaller the Q value. This indicates the less number of iron (III) ions that interact with the sorbitan oleate. One of the biggest factors is due to the alkaline pH (pH> 7), sorbitan oleate will undergo saponification reaction or generally called hydrolysis. Sorbitan oleates which are fatty acid esters will undergo
hydrolysis under alkaline conditions and reshape sorbitan and salts of oleic acid. Since some sorbitan oleates undergo hydrolysis into sorbitan and fatty acid salts, the less iron (III) ion interacts with the remains sorbitan oleates that do not hydrolysis.

A different phenomenon occurred in Figure 8 when pectin was used as an adsorbent. Initially adsorption decreases as it approaches the neutral pH, because the iron (III) ions form the insoluble precipitate Fe(OH)₃. The reason is the iron (III) ion has a very small solubility that is 2 x 10⁻¹₈ M, so that the iron (III) ions will begin to precipitate at pH 7 and will more precipitate when the pH increases. At an alkaline pH (pH > 7), the carboxylic group (-COOH) in pectin becomes negatively charged and it is capable of binding to a positively charged iron metal (III) ion. Although the carboxyl group (-COO⁻) in pectin has better interacting ability, the remaining amount of iron (III) ions is less due to forming Fe(OH)₃ deposits so that the adsorption value at base pH is no greater than at the acidic pH.

Determination of adsorption isotherm between iron(III) ions with sorbitan oleate and pectin was conducted using the optimum conditions (pH, temperature, and time) that had been obtained before. Tests of adsorption isotherms were performed using two types of isotherms that is langmuir isotherms and freundlich isotherms. Figures 9 and 10 are the langmuir isotherm model of iron interaction (III) with sorbitan oleate and pectin.
Figure 10. Langmuir Isotherm of Iron (III) and Pectin

From the equation of line can be determined from the value of $Q_0$ that is the maximum adsorbate coverage value of the monolayer layer (State et al. 2012). The $Q_0$ value of iron adsorption (III) with sorbitan oleate was 15.174 mg / g while the $Q_0$ value of iron adsorption (III) with pectin was 40 mg / g. Figures 11 and 12 are freundlich isotherm models between iron (III) ions with sorbitan oleate and pectin.

Figure 11. Freundlich Isotherm of Iron(III) and Sorbitan Oleate

Figure 12. Freundlich Isotherm of Iron(III) and Pectin

From the langmuir and freundlich isotherms model, the greatest $R^2$ value is found in the freundlich isotherm model so that the adsorption of iron (III) with sorbitan oleate and pectin follows the freundlich isotherm model. From the linear equation of freundlich isotherm model can be determined the value of $K_f$ ie Freundlich characteristic constant and $1 / n$ heterogeneity factor of absorption [8]. The value of $1$
/ n can be changed to a value of n that is the intensity of adsorption. The Kf value or adsorption capacity between iron (III) ions with sorbitan oleate and pectin are 1,193 and 0.8304, respectively.

The Fe (III) interactions of sorbitan oleate and pectin can be seen from the spectrum form of Sorbitan oleic and pectin FTIR respectively before and after mixed with iron (III) solution. Figs 13 and 14 are FTIR spectra between Fe (III) with sorbitan oleate and pectin.

From the data in Figures 13 and 14 it is shown that the iron(III) metal ions are related to the present of O-H group in the sorbitan oleate. In the FTIR spectrum of sorbitan oleate + iron(III) there is a decrease in the intensity of hydroxyl groups when compared with the spectrum of sorbitan oleate without iron(III) ion. Reduced intensity of the O-H spectrum due to iron(III) interactions with O atoms thus reducing the stretching of the O and H bonds on the hydroxyl group of sorbitan oleate. The O atoms of the O-H group will share with their free electron pairs to the iron (III) ions for co-ordinate covalent interactions. One of the reasons why O atoms only interact covalently in coordination with iron(III) ions is that iron(III) ions have greater electropositive value than H⁺ ions so that O atoms have a greater tendency to bind covalently to H⁺ ions than iron(III). The same phenomenon also occurs between the interaction of pectin and iron (III) ions, but the interaction is weaker compared to the interaction of iron (III) ions with sorbitan oleate.
Conclusion
Sorbitan oleates were synthesized in two stages: dehydration of sorbitol into sorbitan and esterification of sorbitan with oleic acid into sorbitan oleate. The acid value obtained in the study with synthesis time 2, 4, 6 and 8 hours were 147.26; 72.93; 50.49 and 24.289 mg KOH / g samples. There was found an optimum condition for sorbitan oleate at 20 °C, 30 minutes, and pH 4; While for pectin at 20 °C, 90 min and pH 5. The iron adsorption process (III) with pectin and sorbitan oleate both followed the Freundlich adsorption isotherm model. The iron adsorption capacity (III) with sorbitan oleate is higher than that of pectin. The interaction between sorbitan oleate and iron (III) is higher than that of iron (III) interaction with pectin.

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