

Characterization of Fe-Chitosan-Succinate-NN'-Methylene Bis-Acrylamide as Ion Imprinted Polymer

M. Suhartini^{1*}, S. Anwar², A. Saefumillah², S. Prayitno¹ and Sudirman³

¹Center for Isotopes and Radiation Application, National Nuclear Energy Agency (BATAN), Jl. Lebak Bulus Raya No. 49, Jakarta 12440, Indonesia.

²FMIPA, University of Indonesia, Jl. Margonda Raya, Depok 16424, Indonesia

³Center for Science Technology of Advanced Materials, National Nuclear Energy Agency (BATAN), Puspipetek Area Serpong, Tangerang Selatan 15314, Indonesia

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ABSTRACT

High level of phosphate in the aquatic environment can reduce the amount of dissolved oxygen in the water which is harmful to the preservation of aquatic ecosystems. However, ion-imprinted polymer (IIP) is available to adsorb tripolyphosphate (TPP). In this study, Fe (III)-chitosan-succinate-tripolyphosphate complex was synthesized with NN'-Methylene Bis-Acrylamide (MBA) as a crosslinking agent and gamma-ray as reaction initiator. The aim of the study is to observe the physical and chemical characteristics of radiation-induced crosslinking of IIP in the presence of MBA. The results show that tripolyphosphate ion adsorption capacity on the Fe-chitosan-succinate-MBA ion-imprinted polymer improved by 75.62 % than that of the non-imprinted polymer. The Differential Scanning Calorimetry (DSC) analysis shows a significant difference in the endothermic, exothermic and glass transitions of chitosan, chitosan-succinate when compared to their complex salts. The Fourier Transform Infra-Red (FTIR) analysis shows the presence of tripolyphosphate groups bonded by Fe-Chitosan-succinate-MBA ion imprinted polymer. Scanning Electron Microscope (SEM) analysis of IIP exhibits a significant difference in surface shapes between IIP with template still within the polymer matrix and after removal.

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INTRODUCTION

Sodium tripolyphosphate (STPP) is a stable inorganic compound used in a variety of household cleaning products (laundry and dishwashing detergents, toilet cleaners, and surface cleaners), human food, animal feed, and ceramics industries. Phosphate concentration at high levels in the aquatic environment can cause the explosion of plants and algae population, eventually reducing the amount of water dissolved oxygen that is harmful to the preservation of marine ecosystems.

Ion-imprinted polymers (IIP) defined as highly selective material which can identify ions in solutions consisting of interference ions with the same matrix. Ion-imprinted polymers (IIP) is similar to molecular printed polymers (MIPS) with different

types of template molecules and ions [1]. The ion-imprinted polymer has specific target adsorption capabilities, high affinity and selectivity for target ions, secure and low-cost manufacturing, reusable and easy to store.

Irradiation technique using gamma rays is capable of producing polymeric materials with rigid structures and high surface area, which can be manufactured with controllable porosity shape and size. Irradiation technique not only has the advantages of high energy induced polymerization, room temperature operation, and controllable polymerization rate, but also can irradiate many samples homogeneously.

Irradiation of chitosan film by using gamma irradiation with irradiation dose up to 50 kGy does not cause degradation. It reflected on IR spectrum, there is no apparent peak of new cluster [2].

*Corresponding author.

E-mail address: meri@batan.go.id

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Mafu et al. has studied the synthesis of arsenic-ion-imprinted polymer (As-IIP) and selenium-ion-imprinted polymer (Se-IIP), where the synthesis was done via bulk polymerization [3]. According to Monier [4] The amine groups in chitosan is the advantage of bonding to either cationic heavy metals via coordination mechanism or anionic metals through ion exchange mechanism. In general, the template molecules are a target compounds in the synthesis process. an ideal template molecule should meet three requirements, one of which is that the template molecule does not contain a dedicated group that can inhibit polymer forming process. The template compound should be chemically stable against the polymer-forming reaction and should provide a functional group that can bind to the function monomer. Most template compounds in molecular imprinting and ion-imprinting, however, are environmentally polluting. In this study, inorganic tripolyphosphate ions were used as the template.-Piletska et al. have reported that excessive amounts of inorganic phosphate have a negative impact on the environment [5].

Long Xu mentioned that IIP must have unique properties, such as nontoxicity, biodegradability, biocompatibility, bioactivity, beside having good physical and mechanical performances [6]. It can be assumed, therefore, that chitosan is a promising alternative as IIP. For this purpose chitosan succinate was synthesized using gamma-ray as reaction initiator in the presence of NN'-methylene bis acrylamide (MBA) as a crosslinking agent and sodium tripolyphosphate as the template. The use of gamma irradiation in ion-imprinted polymers synthesis is expected to produce polymeric materials with rigid structure and high surface area, along with controllable porosity shape and size. Also, it is expected that ion-imprinted Fe-chitosan-succinate produced by irradiation technique increases the tripolyphosphate ion adsorption capacity.

This study observed whether Fe-chitosan-succinate-MBA ion-imprinted polymers synthesized by gamma-ray irradiation has sufficient physical and chemical properties as well as its capability of tripolyphosphate ion adsorption.

EXPERIMENTAL METHODS

The preparation of ion-imprinted polymer was carried out referring to reference [2] as follow: Chitosan was dissolved in 1 % acetic acid solution. The solution of succinic anhydride in pyridine was added while stirring. The resulting chelates were then placed on a Petri dish and dried at 50 °C for

24 hours. Further, the sample was dissolved in 5 % acetic acid. The $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to this solution. Sodium tripolyphosphate was added to the Fe (III) mixture-chitosan succinic. This mixture solution was added to 1 M NaOH solution. The solution was stirred for 12 hours and subsequently dried. To the dried solution was added MBA of 1 %, 3 %, and 5 % and without an MBA as control. The sample were then irradiated with gamma rays from Co-60 with a dose rate of 1 kGy/hour and a variation of irradiation dose of 0 kGy; 10 kGy; 20 kGy; 30 kGy; 40 kGy and 50 kGy. After the irradiation, the tripolyphosphate ion was removed from the ion-imprinted polymer by the addition of 10 mL KOH 1 M solution.

The degree of crosslinking was determined according to reference [2].

Functional group analysis using FTIR spectrophotometer

The samples of chitosan, IIP, non IIP and eluted IIP were finely grounded and mixed with KBr powder (1: 200) and then fed into a stainless steel container. The analysis was performed in a range of 4000-500 cm^{-1} wavenumbers with a resolution of 4 cm^{-1} .

Thermal analysis using DSC

Some samples of Chitosan, Chitosan succinate and IIP were placed on aluminium plates and then pressed and inserted into a DSC instrument. Heating was done from room temperature to 500 °C.

RESULTS AND DISCUSSION

Modified of chitosan succinate

Figure 1 shows the reaction mechanism during the modifying of chitosan to chitosan succinate.

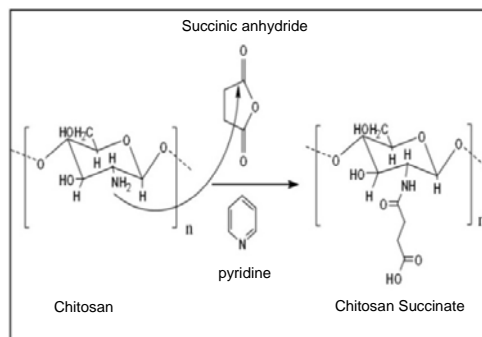


Fig. 1. Reaction mechanism of chitosan succinate from chitosan and succinic anhydride [7].

Conjugate reactions occur in the presence of succinic anhydride. The succinic anhydride undergoes strong electrophilic reaction with nucleophilic amine groups in chitosan, causing a selective acylation reaction in the amine group. These reactions may also be due to the fact that the nucleophilic character of the amine group is stronger than the adjacent hydroxyl group [8]. The reaction mechanism occurs through a single-stage: the nucleophilic amine group attacks the carbon in the carbonyl group of the anhydrous succinate. The release of the leaving group will be accompanied by the binding of the amine group [9]. Pyridine is used as an acylation catalyst because, despite having a nitrogen atom, pyridine does not react with anhydrous succinate as pyridine has been stabilized through the resonance in its molecular structure.

The soluble chitosan dissolves at a solution pH below four and above seven but does not dissolve completely at pH between 4 to 7. The chitosan-succinate dissolves at pH below 4 through-the protonation of the amino group ($-\text{NH}-\text{NH}_2^+$), whereas the chitosan succinate dissolves at pH above 7 due to the change of the carboxyl group into carboxylic ions ($-\text{COOH}$ to $-\text{COO}^-$). At a pH between 4 to 7, carboxyl groups undergo partial ionization and are at isoelectric state, thus decreasing the solubility of chitosan succinate [9].

The crosslinking yield and adsorption capacity

The crosslinking yields of imprinted polymer sample are presented in Table 1.

Table 1. The crosslinking yield and adsorption capacity of imprinted polymer at irradiation dose of 20 kGy.

	Crosslinking Yield (%)	Adsorption Capacity ($\mu\text{g/g}$) $\times 10^3$
NIP-Non MBA		3.0
NIP-MBA 1 %	50.50	3.2
IIP-MBA 1 %	58.88	5.0
IIP-MBA 3 %	62.09	4.0
IIP-MBA 5 %	81.19	3.2

According to Table 1, the highest percentage of crosslinking yield is at MBA-5 %. Higher crosslinking yield of the polymer means higher insolubility, more significant polymer surface density and tighter porous polymer, but does not correlate to adsorption capacity. It is also indicated that the non-imprinted polymer-MBA (NIP-MBA) obtained has a lower degree of crosslink degree than the IIP. Tighter polymer pores cause the

tripolyphosphate ion to be less capable of moving freely to polymer pores [10].

It can be seen from Table 1 that the highest adsorption obtained is at ion-imprinted polymer with 1 % MBA. This correlates with the observation by Baroroh et al. that the increasing concentration of MBA increases the polymer surface density and decrease porosity [11]. At fixed tripolyphosphate ion concentrations, the adsorption capacity will have a direct proportion to the concentration of the crosslinking agent.

The decrease in adsorption capacity, due to increased concentration of MBA, occurs because the polymer forms a denser tissue so that the pores formed become smaller, causing difficulty of the polymer in adsorption [11].

Variation of irradiation dose with 1 % MBA is shown in Fig. 2.

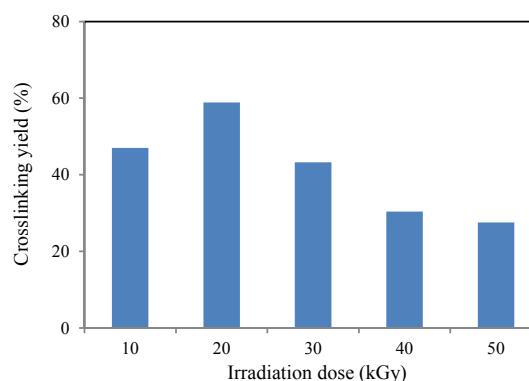


Fig. 2. The crosslinking yield of IIP with 1 % MBA at different irradiation dose [2].

Figure 2 shows that the highest crosslinking yield is obtained at an irradiation dose of 20 kGy.

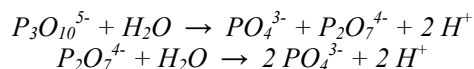
Adsorption study of ion tripolyphosphate

The data of the conversion of tripolyphosphate to phosphate by destruction method is presented in Table 2.

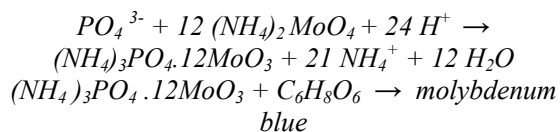
Table 2. Conversion of tripolyphosphate to phosphate by the destruction method.

Sample	Conversion	Fosfat concentration (ppm)
1 ppm TPP	0.0088	0.91
2 ppm TPP	0.0127	1.67
3 ppm TPP	0.0165	2.40
4 ppm TPP	0.0218	3.43

The decomposition reaction mechanism of tripolyphosphate ions into phosphate occurs in the destruction process, which can be described by the reaction mechanism below.



Where $P_3O_{10}^{5-}$ is a triphosphate ion, PO_4^{3-} is an orthophosphate ion, and $P_2O_7^{4-}$ is a pyrophosphate ion. Phosphate ion can be analyzed by ascorbic acid method as follows:



Adding ammonium molybdate to the phosphate solution will give $(NH_4)_3PO_4 \cdot 12MoO_3$ [10]. In this research the $(NH_4)_3PO_4 \cdot 12MoO_3$ was reduced by ascorbic acid from Mo (VI) to Mo (V) (phosphomolybdenum) resulting in blue colour in the solution and then this solution was measured at a wavelength of 886 nm (the wavelength values were obtained from the maximum absorbance measurement). The phosphate concentration can be determined by correlating with the standard phosphate solution regression equation.

Effect of NN'-Methylene Bis-Acrylamide (MBA)

Figure 3 shows that, the highest adsorption is obtained in an ion-imprinted polymer with 1 % MBA. It has been understood that at increasing concentration of MBA, the polymer surface density becomes smoother because of less porous formed [11], so the access of adsorption becomes more difficult than that of the access of adsorption in the imprinted ion with a 1 % MBA concentration. At fixed triphosphate ion concentrations, the adsorption capacity has a direct proportion to the concentrations of crosslinking agent.

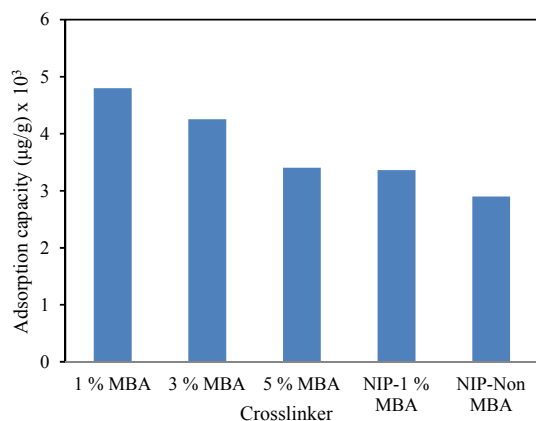


Fig. 3. NN'-Methylene Bis-Acrylamide (MBA) concentration to TPP adsorption capacity.

Based on the above results, it is known that the highest adsorption capacity obtained at ion-imprinted polymer (IIP) with 1 % MBA which reached 4798 µg of triphosphate adsorbed per g of IIP, improved by 75,62 % compared to that of non imprinted polymer. This is because the high concentration of MBA crosslinking agent in the polymer during irradiation causes an increase in the crosslinking yield of the polymer, which eventually makes the surface pores of the polymer become denser. This phenomena causes the triphosphate ion template to become narrow and not fully formed, which is turn to decrease the adsorption of triphosphate ions.

Figure 4 shows the schematic of molecular imprinting, where a complex with a template molecule is formed by monomers, then the complexes are joined by a crosslinking agent. After polymerization the template is removed by chemical reaction, and the imprinted polymer is ready to be applied [6].

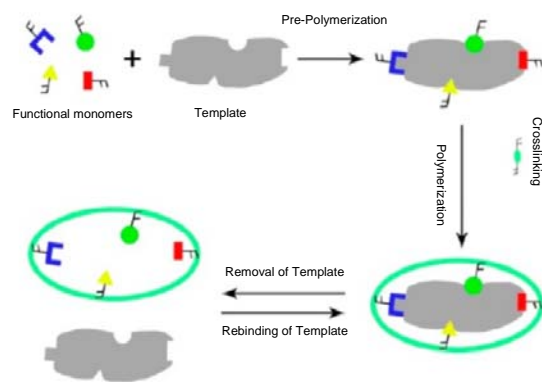


Fig. 4. The schematic of molecular imprinting [6].

Thermal properties analysis

Differential Scanning Calorimetry (DSC) was used for thermal properties analysis. The endothermic peak temperature of chitosan is at around 89 °C and the exothermic peak at 312 °C [13] while the endothermic peak temperature of chitosan succinate at around 70 °C and exothermic peak at 410 °C. The endothermic peak temperatures of the uncrosslinked polymer is at 152 °C, and there will be an increase in endothermic peak temperature of crosslinked complex polymers to 159 °C as shown in Fig. 5.

Through the results of thermal analysis of chitosan and chitosan succinate shown in Figs. 5a and 5b, the peak of endothermic, exothermic and glass transition (T_g) of the sample can be identified. The first endothermic peak indicates dehydration process due to heating. The exothermic peak indicates a change in the shape of the material from

a molten state to stable because of the cooling process while the glass transition shows a reversible change of the amorphous material from hard/rigid state to liquid/plastic state.

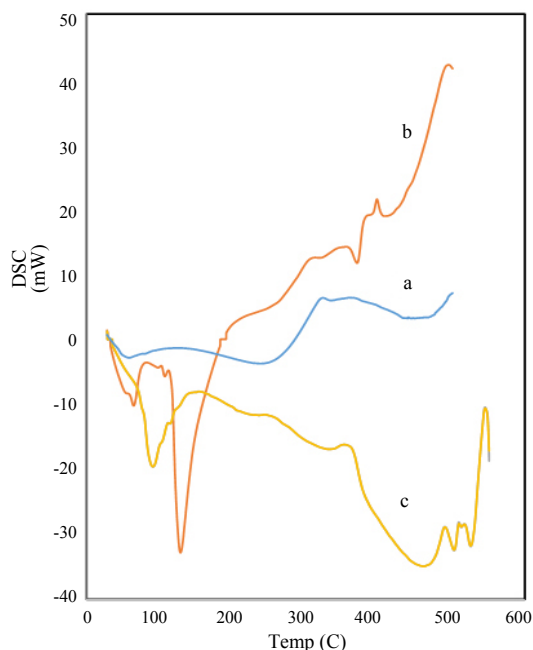


Fig. 5. Differential Scanning Calorimetry (DSC) analysis of (a) chitosan, (b) chitosan succinate, (c) Fe-chitosan-succinate.

Figure 5a shows the thermal analysis of chitosan. It can be seen that the endothermic peak temperature occurs at about 58 °C. The exothermic peak occurs at 324 °C, where at this temperature the material changes from molten state to solid because the glass transition temperature (T_g) of chitosan is around 170 °C. Based on reference [13], endothermic peak temperature of chitosan occurs at 89 °C and an exothermic peak occurs at 312 °C. The transition temperature of chitosan glass based on research by Kusumawardani & Saefumillah is at 180 °C [8].

Figure 5b shows the chitosan succinate thermal analysis results. It can be seen that the endothermic peak temperatures of chitosan succinate at 38 °C to 154 °C, exothermic peak at 398 °C while the glass transition temperature occurs at about 290 °C. Based on research by Kusumardani and Saefumillah [8], the endothermic peak temperature of chitosan succinate occurs around 40-150 °C, exothermic peak at 410 °C and glass transition (T_g) at 260 °C. The difference in the temperature identification of endothermic, exothermic, and glass transition on chitosan and chitosan-succinate indicates the existence of structural change in chitosan and chitosan succinate during synthesis.

Figure 5c shows that the Fe-chitosan-succinate complex has an endothermic peak at

91 °C, and the endothermic peak is a waterlogging condition occurring temperature 77 °C to 115 °C. The exothermic peak occurring at 353 °C represents a change in the shape of the material from molten to solid while the glass transition (T_g) occurs at 230 °C. The endothermic, exothermic and glass transition peaks occur at about 100 °C, 360 °C and 180 °C respectively.

Fourier Transform Infra-Red (FTIR) analysis

Fourier Transform Infra-Red (FTIR) was used to analyze the functional group. In the case of N-acylation reaction, the succinyl group of succinic anhydride will enter into the amine group on chitosan so that it will form amide group and carboxylic group on chitosan succinate. The absorption band which appears in the wavenumber of 1660-1670 cm^{-1} , 3200-3650 cm^{-1} and 1710-1720 cm^{-1} indicate a carbonyl amide group, the presence of hydroxyl carboxylic of succinyl group, and the formation of C=O carboxyl respectively.

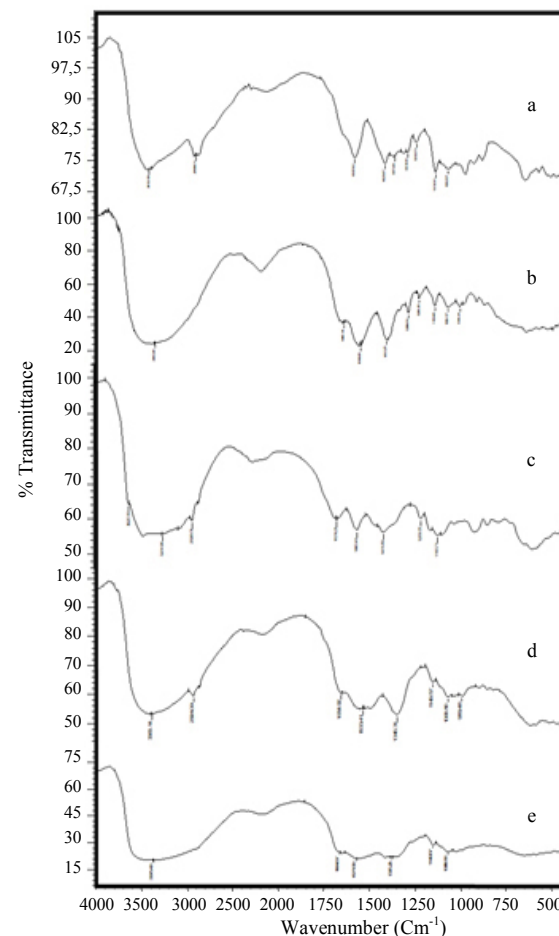


Fig. 6. The FTIR spectrum of (a) chitosan, (b) chitosan-succinate, (c) Fe-chitosan-succinate-tripolyphosphate, (d) Fe-chitosan-succinate (Elution Result), (e) non-imprinted Fe-chitosan-succinate polymers.

The chitosan spectrum presented in Fig. 6a shows the absorption band in the wavenumber of 1587 cm^{-1} indicates the presence of the NH bond bending. The uptake at 1423 cm^{-1} denotes the presence of CN stretching bonds, whereas uptake of about 2100 cm^{-1} and 1373 cm^{-1} denotes the presence of a methyl group. An absorption area of 3412 cm^{-1} indicates the presence of stretching of the hydroxyl group (OH), and the region of 2899 cm^{-1} indicates the presence of C-H stretching groups [12].

Meanwhile, the chitosan-succinate spectra presented in Fig. 6b show the presence of stretching of hydroxy (OH) carboxylic group at 3350 cm^{-1} , stretching carbonyl amide (C = O) at 1649 cm^{-1} , bending bond (NH) at 1557 cm^{-1} , stretching bond CN at 1416 cm^{-1} . The absorption peaks of carbonyl amide (C = O) appear on wave numbers $1674\text{-}1681\text{ cm}^{-1}$. This shows the substitution of carboxylic groups of chitosan [12].

The FTIR spectrum of chitosan and chitosan succinate as presented in Figs. 6a and 6b show that NH bending bond shifts from 1587 cm^{-1} to 1557 cm^{-1} and CN bond shifts from 1423 cm^{-1} to 1416 cm^{-1} as generally known that the bonding frequency is influenced by bonding strength and bonded atomic mass. Because the atomic mass factor of both is the same, bond strength factor results in shift. The strength of N-H and C-N bonds are stronger in chitosan molecules than that in chitosan succinate due to the presence of carbonyl groups in the succinate, which is electron-pulling and can weaken the N-H bond between the chitosan- succinate.

The Fe-chitosan-succinate-tripolyphosphate polymer spectrum appearing at $3200\text{-}3650\text{ cm}^{-1}$ (Fig. 6c) indicates the presence of stretching out O-H from carboxylates. The wave number 2926 cm^{-1} , 1674 cm^{-1} , 1560 cm^{-1} , and 1412 cm^{-1} indicates the presence of stretching CH, the presence of stretching of carbonyl amide (C=O), the presence of bending amide (NH), and the presence of CN stretching respectively. Meanwhile, uptake at $1203\text{-}1119\text{ cm}^{-1}$ shows the presence from stretching of clusters P=O and P-O and uptake at 540 cm^{-1} indicates the presence of P-OH. The characteristic of P=O and P-O absorption occurs at $1210\text{-}1082\text{ cm}^{-1}$ and for P-OH stretching at $490\text{-}970\text{ cm}^{-1}$ [14]. These results imply that the presence of tripolyphosphate groups is bonded by Fe (III) -chitosan-succinate.

The spectrum of imprinted polymer Fe-chitosan-succinate-tripolyphosphate that has been eluted can be seen in Fig. 6d.

According to Fig. 6d, the absence of absorption at 1203 cm^{-1} indicates the absence P=O and P-O, and the absence of absorption at 540 cm^{-1} indicates the absence of P-OH, suggesting that

addition of 10 ml of 1 M KOH solution to the polymer can remove the tripolyphosphate from the polymer. Figure 6e is the FTIR characterization results of non-imprinted polymer (NIP), which was used as a control. The figure showed that in the range of 1203 cm^{-1} and $490\text{-}970\text{ cm}^{-1}$ there is no peak, which indicates the absence of tripolyphosphate groups.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy is one of the best method to study the polymer morphology. Through SEM analysis, both structure of surface and cross-section of a polymer can be determined. Besides, SEM can also be used to study pore distribution, pore geometry, pore size and porosity on the surface.

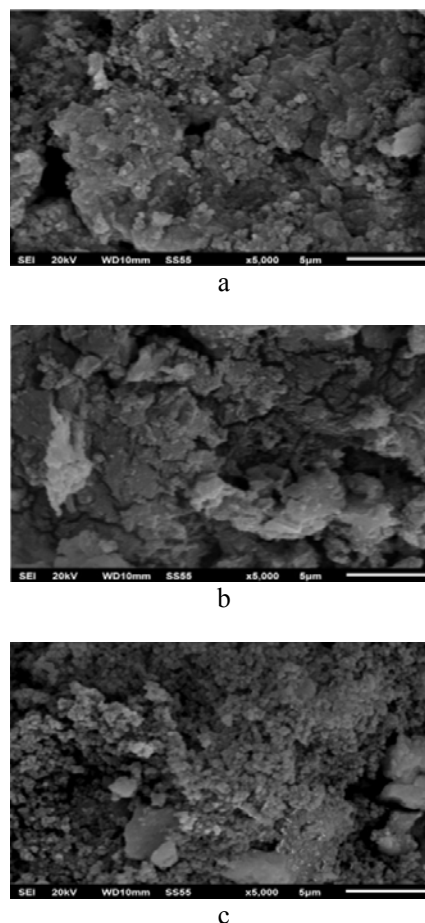


Fig. 7. Scanning Electron Microscopy Analysis of (a) NIP-1 % MBA-20 kGy, (b) IIP- 1 % MBA-20 kGy, (c) Eluted IIP-1 % MBA-20 kGy, Magnification 5000x.

A back scatter detector was used for the surface and morphology investigation. Figure 7 shows the micrograph of the non imprinted polymer (NIP)-1 % MBA (Fig. 7a) and ion-imprinted

polymer (IIP)-1 % MBA (Fig. 7b), where both of the polymer were irradiated with an irradiation dose of 20 kGy. It can be seen from Figs. 7a and 7b that there is a significant difference on the surface of the NIP compared to the IIP. The NIP surface appears to be lacking of uniform pores and more rough, whereas the resultant IIP shows uniform, smooth surface morphology, more even and dense, as shown in Fig. 7b. Subsequently, after the template had been removed from the polymer matrix, it was found that obvious pores were formed, and the surface was more rough in the eluted polymer matrix, as can be seen in Fig. 7c. The different surface shapes between the IIP and the eluted IIP, i.e., IIP with the template still within the polymer matrix and after removal, are evidence.

CONCLUSION

The synthesis of ion-imprinted Fe-chitosan-succinate polymer with MBA as crosslinking agent can be done by chitosan modification method. The tripolyphosphate ion adsorption capacity on the Fe-chitosan-succinate-MBA ion-imprinted polymer was greater significantly than that of the non-imprinted polymer. There is a significant difference in endothermic, exothermic and glass transition peak in chitosan, chitosan-succinate and Fe-chitosan-succinate-MBA. Tripolyphosphate can be eluted by using a potassium hydroxide solution. Obtained that there was different surface shapes between IIP and eluted IIP.

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M. Suhartini^{1*} is the main contributor of this Paper.

REFERENCES

1. M. Cejner and R. Dobrowolski, *Umschem* **70** (2015) 67.
2. S. Anwar, A. Saefumillah and M. Suhartini, *J. Phys.: Conf. Ser.* **1442** (2020) 012053.
3. L.D. Mafu, B.B. Mamba and T.A.M. Msagati, *J. Saudi Chem. Soc.* **20** (2016) 594.
4. M. Monier and D.A. Abdel-Latif, *Int. J. Biol. Macromol.* **105** (2017) 777.
5. E.V. Piletska, A.R. Guerreiro, M. Whitcombe, *et al.*, *Macromolecules* **42** (2009) 4921.
6. L. Xu, Y.A Huang, Q.J. Zhu *et al.*, *Int. J. Mol. Sci.* **16** (2015) 18328.
7. H.S. AlKhatib, K.M. Aiedeh, Y. Bustanji *et al.*, *Eur. J. Pharm. Biopharm.* **70** (2008) 804.
8. D.A. Kusumawardani and A. Saefumillah, *Studi pembuatan Ion Imprinted Polymer untuk penyerapan Sodium Tripolifosfat (STTP)*, Thesis, Universitas Indonesia (2013). (in Indonesian)
9. T.M. Tamer, M.A. Hasan, A.M. Omer *et al.*, *Carbohydr. Polym.* **169** (2017) 441.
10. K. Aiedeh and M.O. Taha, *Arch. Pharm. Pharm. Med. Chem.* **332** (1999) 103.
11. U. Baroroh, A. Irwan and M. Mahmudah, *Jurnal Sains dan Terapan Kimia* **8** (2014) 37. (in Indonesian)
12. K. Vijayalakshmi, B.M. Devi, P.N. Sudha *et al.*, *J. Nanomed. Nanotechnol.* **7** (2016) 1.
13. T.R. Gatot, *Jurnal Kimia Kemasan* **36** (2014) 183. (in Indonesian)
14. A.I. Martityan and L.A. Nersesian, *Synthesis and Analysis of Sodium Tripolyphosphate Peroxo Solvate*, Proceedings of the Yerevan State University, Chemistry and Biology **2** (2015) 18.