Synthesis of ion-imprinted polymer with gamma irradiation for the adsorption of Tripolyphosphate

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Abstract. One method of separating tripolyphosphate ion uses ion-imprinted polymer. Chitosan-succinate, tripolyphosphate and methylene bis acrylamida (MBA) were used as the complexing polymer, template, and crosslinker agent, respectively. In the first step, Fe(III)-chitosan-succinate-tripolyphosphate was formed. In the second step, Fe(III)-chitosan-succinate-tripolyphosphate was crosslinked by MBA and irradiated by gamma rays. Then, tripolyphosphate ion was removed with KOH solution to form a selective cavity for tripolyphosphate ion in the ion-imprinted polymer (IIP). Based on the results of this study, the optimum adsorption of tripolyphosphate ion was found at an MBA crosslinker concentration of 1%, pH 2, irradiation dose 20 kGy, and a tripolyphosphate ion concentration of 1 ppm. This study also included experimental adsorption of tripolyphosphate ion on non-imprinted polymer (NIP-MBA) and an evaluation of the effect of interference ions. The resulting adsorption of tripolyphosphate ion on IIP was found to be higher than those of non-imprinted polymer. The adsorption percentages were found to be 94 % for IIP and 14 % for NIP-MBA. Chloride ion (Cl\textsuperscript{−}) provided greater interference in the adsorption process of tripolyphosphate ion compared to carbonate ions. The percent adsorptions of tripolyphosphates were estimated to be 57.71 % in the presence Cl\textsuperscript{−} and 68.28 % in the presence CO\textsubscript{3}\textsuperscript{2−} ion.

Keywords: ion-imprinted polymer, gamma irradiation, Tripolyphosphate

1. Introduction
Tripolyphosphate ion (P\textsubscript{3}O\textsubscript{10}\textsuperscript{4−}) in sodium tripolyphosphate (Na\textsubscript{2}P\textsubscript{3}O\textsubscript{10}) is commonly used in detergents (domestic and industry). The tripolyphosphate ion in the environment can be hydrolyzed to produce HPO\textsubscript{4}\textsuperscript{2−} and HPO\textsubscript{3}\textsuperscript{−} orthophosphates [1]. The disposal of detergent wastewater into aquatic environments leads to an increase in tripolyphosphate ions and indirectly affects the phosphate levels. High levels of phosphate in the water caused the population explosion of plants and Algae (eupr), thus reducing the amount of dissolved oxygen in water that is harmful to aquatic ecosystems [2]. One method that is capable of separating tripolyphosphate ion is ion-imprinted polymer. In an ion-imprinted process, a template ion or analytes join with one or more of polymer chains to form a complex.

Then, the complex is joined with a crosslinking agent to produce the resin. Temporal displacement produces a hollowing on the polymer, which is reused selectively as binding templates from a chemical mixture solution [3]. This study examines the relatively new synthesis of ion-imprinted polymer (IIP) for adsorption as well as preconcentration of tripolyphosphate ions. Based on information provided by Ozkütük et al. [3] regarding IIP Fe-chitosan-succinate and the crosslinker epichlorohydrin with research reported by Juliana [4], ion-imprinted Fe-chitosan-succinate and crosslinker methylene bis acrylamide (MBA) has been successfully used in the synthesis of IIP, and
the adsorption of phosphate is quite good. However, based on information reported in Kusumawardani [5], tripolyphosphate ion adsorption by IIP Fe-chitosan-succinate is still less than the maximum triplyphosphate ion adsorption.

Therefore, the development of a method that uses gamma ray irradiation using variations of crosslinker MBA and TMAIC represent a promising solution. In particular, the complex of Fe (III)-chitosan-succinate has successfully synthesized and reacted with sodium triplyphosphate and crosslinked with MBA, and subsequently irradiated with gamma rays is possible. Several studies using gamma rays in molecules and ion-imprinted have been performed. Uezu et al. [6] and Biju et al. [7] have studied the effects of polymerization by gamma irradiation on the selectivity of IIPs. Kala et al. [8] synthesized erbium (III) from a number of monomer-crosslinker pairs with gamma irradiation. Several studies of polymer synthesis imprinted with organic template molecules, such as methanol, testosterone and cholesterol, have been performed and published. Based on research in Erizal et al. [9], doses of 10–50 kGy did not result in the degradation in chitosan until irradiation reached 50 kGy.

2. Experimental

2.1. Experiment instruments
Measurement instruments used in this study included a Irradiator gamma 4000 A with a source of Cobalt-60, a Spectrophotometer UV–Vis, a pH-meter, DSC, and Fourier Transform Infrared (FTIR).

2.2. Substances used in the experiment
Chitosan, succinic anhydride, MBA, TMAIC, Na.CO, NaOH, NaCl, Fe(NO₃)₃.9H₂O, sodium triplyphosphate, acetic acid, pyridine, and KOH were utilized in the experiments, and all were of a pro analysis grade.

2.3. Preparation of chitosan-succinate material
At room temperature, 1 g of chitosan was completely dissolved in 200 mL of 1% acetic acid solution, and a solution of 0.625 g of succinic anhydride in 5 mL of pyridine was dripped with stirring. The pH value of the reaction was maintained at pH 7 by the addition of a few drops of 1 M NaOH. Then, the resulting mixture was poured into a petri dish and dried at 50 °C to obtain chitosan-succinate as a solid layer.

2.4. Preparation of triplyphosphate-complex-chitosan succinate
At room temperature, 1 g chitosan was completely dissolved in 5 % acetic acid and 2 g of Fe(NO₃)₃.9H₂O was added gradually introduced to this solution and well stirred. The Fe(III) ions introduce by mixing with amide groups of chitosan-succinate, and as many as 8.86 g of sodium triplyphosphate were added slowly to the solution of Fe(III)-chitosan-succinate. This mixture was slowly added to 150 mL of 1M NaOH solution. Then, the solution was stirred continuously for 12 h. After that it was filtered, producing the yellow suspension mixture and continued for drying it in the oven. The resulting complexes of chitosan-succinate-triplyphosphate were polymerized using 1 % : 3 % : 5 % MBA, and subsequently irradiated with gamma rays. IIP was irradiated by gamma rays with dose variations of 0 kGy, 10 kGy, 20 kGy, 30 kGy, 40 kGy, and 50 kGy. Then, the triplyphosphate ion was removed from the IIP with the addition of 10 mL KOH 1 M solution.

2.5. Determination of crosslinking degree
The degree of crosslinking of this IIP was determined by means of extraction. A total of 20 mg of IIP was soaked in 50 mL of 5 % acetic acid (v/v) for 24 h, then dried in an oven at a temperature of 50 °C–60 °C. Furthermore, the dry weight prior to the soaking and dry weight after the immersion step was measured. The percentage of crosslinks can be expressed by equation (1):

\[(\%) \ DC = \frac{W_a}{W_b} \times 100\% \]  \hspace{1cm} (1)

where Wa is referred to the dry weight of a IIP after the immersion and Wb is the dry weight of IIP prior to submersion.

2.6. Adsorption/desorption studies
2.6.1. Adsorption studies. The effects of pH and the initial concentrations of STPP or Na₃PO₄, on the adsorption rate and adsorption capacity were investigated in batch method of adsorption equilibrium experiments. The effect of pH on the adsorption rate of the phosphate-imprinted polymer was investigated in a pH range of 2.0–8.0 at 25 °C. The maximum adsorption of this experiment was observed at pH of 2.0, and this pH was applied for all further experiments. The suspensions were brought to the targeted pH by adding a few drops of NaOH or HNO₃ solutions. In all conducted experiments, the polymer concentration was kept being constant at 5 mg/10 mL. The effect of the initial template ion concentration on the adsorption was studied at a pH 2.0 as described above. The concentration of this triplyphosphate ions in the adsorption medium was varied between 1 to 4 ppm.

Competitive adsorption of triplyphosphate/chloride and triplyphosphate/carbonate from their mixture was also investigated for interference other anions effect in this type of batch system experiment. A 10 mL solution containing 3 mg L⁻¹ from each anion was treated with the triplyphosphate-imprinted microparticles polymer at the pH of 2.0 at ambient temperature. After reaching adsorption equilibrium, the anions concentration in the remaining solution was measured with a UV spectrophotometer at 886 nm with ascorbic acid using phosphomolybdenum blue complex formation method, while the sample was then destructed with perchlorate acid and sulphate acid before measurement. The amount of adsored triplyphosphate ion was obtained using the following expression (equation (2)):

\[ Q = \frac{(C_{\text{in}} - C_{\text{out}}) V}{M} \]  

where \( Q \) is the quantity of triplyphosphate ions adsorbed onto the mass of this IIP (mg g⁻¹); \( C_{\text{in}} \) and \( C_{\text{out}} \) are the concentrations of the triplyphosphate in the initial solution and in the aqueous medium after adsorption, respectively (mg L⁻¹); \( V \) is the volume of the aqueous phase (mL); \( M \) is the amount of polymer (g).

2.6.2. Desorption and reusability. In a 10 mL solution that contain 3 ppm of triplyphosphate ion, 5 mg of the imprinted polymer was prepared for the adsorption process. Then, adsorbed triplyphosphate anions were eluted by contacting of the imprinted polymer with 1M KOH solution for 30 min. The desorption ratio was calculated using equation (3):

\[ \text{Desorption ratio} = \frac{\text{amount of ions desorbed to the elution medium}}{\text{amount of ions adsorbed onto the sorbent}} \times 100 \]  

The adsorption-desorption cycle of experiment was repeated seven times for the study of reusability of the triplyphosphate-imprinted polymers. The imprinted polymer was washed several times with 1M KOH solutions and demineralized water oxidation after each use before being reloaded again.

3. Results and discussion

3.1. Characterization of Fe-chitosan-succinate complex polymer

Fe-chitosan-succinate was crosslinked using 1%, 3%, and 5% MBA, and subsequently irradiated by gamma rays. In the spectrum of Fe-chitosan-succinate polymer, absorption was observed at wavenumber of ~1674 cm⁻¹ and at 1560 cm⁻¹. On the spectrum of Fe-chitosan-succinate that bind triplyphosphate, a phosphate band was observed at around 564 cm⁻¹ and 1203–1119 cm⁻¹. The absorption at wave numbers 3200–3500 cm⁻¹ represents the presence of OH and the wavenumber of 1412 cm⁻¹ shows the presence of C–N. These results indicate the presence of phosphate groups bound by Fe (III)-chitosan-succinate. Based on Nie et al. [10], the characteristic absorption of P=O and P–O occurred in 1210–1082 cm⁻¹. Since the control group was synthesized with the non-imprinted polymer, no peak appeared at 564 cm⁻¹, which indicated the absence of phosphate groups.

In figure 1a, the highest crosslinked degree at a MBA concentration of 5% was 81.19%, and greater degrees of crosslinking are increasingly insoluble with large membrane density or less porosity and less expanding polymer. However, it does not mean that the greater the degree of crosslinking, the better the adsorption process. Based on the percentage adsorption effects on the variation of crosslinker concentration, it is known that the optimum condition is achieved at 1% MBA, which is due to the increasingly tightly polymer pores causing less triplyphosphate ion to move freely. The crosslinking of the non-imprinted form was 0.25%, which is soluble in 5% acetic acid. Varied irradiation dosages with 1% concentration of MBA obtained the crosslinking percentages depicted in figure 1b. As seen in figure 1b, an irradiation of 20 KGy obtained the largest % degree of crosslinking that is 58.88%.
3.2. Adsorption study of tripolyphosphate

3.2.1. Determination of optimum MBA concentration and irradiated dosage. In this study, the variation of MBA concentration to determine the optimum concentration and based on the known optimum concentration at 1% MBA. These results are presented in figure 2a. As depicted in figure 2a, the highest adsorption percentage for crosslinker variations was obtained at 1% MBA, whereas the adsorption percentages associated with the non-imprinted version were 56.07% for NIP-1% MBA and 48.32% for non-imprinted polymer (NIP) without MBA. Based on Kusumardani’s research [5], the known maximum adsorption percentage obtained was obtained 1% MBA concentration. Based on the above results, the optimum irradiation conditions occur at 20 KGy (figure 2b). This was because the degree of crosslinking was the highest at 20 kGy, which corresponds to adsorption percentage of 58.88%. Based on research by Erizal et al. [9], the irradiation of chitosan from 10 kGy up to 50 KGy does not cause degradation of the chitosan polymer, so that the adsorption trend from 10 to 50 kGy was not due to the degradation of chitosan, but due to the non-maximum crosslinking process. This is referred to as the percentage of crosslink from the previous data.

3.2.2. Determination of optimum pH and tripolyphosphate concentration. The experiment of pH effect on the adsorption of tripolyphosphate is presented in figure 3a, which indicates a large affinity in acidic conditions (a pH of 2 or less), whereas figure 3b depicts the phosphate adsorption in Fe-chitosan-succinate-phosphate at an optimum pH 2.

3.2.3. Determination of the influence of the interfering ion. The competition for P.O_4^{3-}/Cl^- and P.O_4^{3-}/CO_3^{2-} adsorption as evaluated from each paired mixture of interference were studied in the batch system method. The adsorption capacity of imprinted and the control of non-imprinted polymer-tripolyphosphate for CO_3^{2-} and Cl^- anions at a concentration of 3 ppm and a pH 2 are presented in figure 4.
Figure 4. Influence of interference ion against % adsorption

In accordance with figure 4, the decrease in adsorption of tripolyphosphate in the presence of disruption ions created by the adsorption of CO$_3^{2-}$ and Cl$^-$ disrupting ions can be expressed as % adsorptions of tripolyphosphates, with 57.71 % for Cl$^-$ ion and 68.8 % for CO$_3^{2-}$ ion. These results are due to the Cl$^-$ ion being smaller than CO$_3^{2-}$ ion, which makes it easier to move even though the CO$_3^{2-}$ ion’s charge is large.

4. Conclusions
The results of this study concluded that there are several important insights about polymer ion-imprinted Fe-chitosan-succinate crosslinked with MBA synthesized via chitosan modification and irradiated with gamma rays. The resulting IIP provides a higher percent adsorption than the NIP, and the optimum concentration of crosslinker MBA was determined to be 1% at a pH of 2, an irradiation dose at 20 Kgy, and a concentration of STPP of 1 ppm with an adsorption percentage of 94.02 %.

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