Synthesis and characterization of zeolite-g-polyacrylamide (Zeolite-g-PAAM) by using simultaneous irradiation technique

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Abstract. In this study, we synthesized the adsorbent based zeolite as an adsorbent for toxic metal removal. The modified zeolite adsorbent has been successfully synthesized using polymerization radiation technique by gamma rays. The monomer of acrylamide was applied to be grafted onto zeolite. The irradiation doses used in this study were 10−75 kGy and we obtained the optimum dose for synthesizing the zeolite-g-polyacrylamide by using the simultaneous irradiation technique was 25 kGy, with 99.88% and 48.01% for the gel fraction and degree of grafting, respectively. The zeolite-g-polyacrylamide were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Scanning Electron Microscope (SEM).

1. Introduction
In the recent past, polymeric adsorbents have arisen as a potential alternative to replace activated carbon. Polymeric adsorbents are preferable to other solid adsorbents due to their vast surface area, suitable to be functionalized for resulting selective adsorbent, and feasible regeneration process [1]. Recently, polyacrylamide (PAAM) has been utilized as an adsorbent for toxic metal removal [1-4]. PAAM has enormous water adsorption capacity. However, the adsorbent generated from the acrylamide monomer has low physical and mechanical properties. To overcome these limitations, more recently, promising organic-inorganic hybrid polymers have been used for the removal of toxic species [6,7]. In these compounds, the functional variation of organic materials is combined with advantages of a thermally stable and robust inorganic substrate, resulting in strong binding affinities toward selected metal ions and relatively high metal ion adsorption capacities. Functionalized hybrid polymeric materials as adsorbent are regarded as one of the most effective techniques because metal ions can be chemically bonded by the organic-inorganic polymer hybrids. These kinds of materials often present the best properties of each of its components in a synergic way and have high performances of physical, chemical and mechanical properties [8,9]. The hybrid PAAM with some inorganic material such as silica, hydroxyapatite and synthetic zeolite has been reported by several authors [5-7]. However, the information regarding the characterization of PAAM onto natural zeolite is still very limited. In this work, the characteristics of the hybrid Zeolite-g-PAAM that synthesized by using simultaneous gamma radiation-induced graft copolymerization are elaborated in detail.
2. Methodology

2.1. Materials
The clinoptilolites type zeolite originated from the South Lampung region was supplied by Minatama Company, acrylamide monomer (C₃H₅NO) was kindly supplied by Merck, and demineralization water was used as the solvent.

2.2. Methods
The zeolite was weight as 500 g. The zeolite furthermore was washed using demineralization water for 3×8 hours in the Soxhlet apparatus. The used water was replaced per 8 hours. The washed zeolite then dried, ground and screened to get 60 mesh size.

The acrylamide solution (C₃H₅NO) in H₂O with a concentration of 20, 30 and 40% (w/v) were prepared in 100 mL volumetric flask for each respectively. Furthermore, 10 g zeolite powder was weighed and put on the 5×5 cm of the poly-ethylene plastic bag, followed by adding 10 g of acrylamide solution for each concentration and mixed homogenously. The plastic bag then sealed and subjected to gamma irradiation (Co-60) simultaneously with the dose ranges of 10 to 75 kGy. The same procedure was performed to the acrylamide solution without zeolites which irradiated as control. The irradiated samples of zeolite-g-PAAM hybrid and PAAM gel then dried at 50 °C for 24 hours until they reached the stable weight for further examination. For gel fraction measurement, both of zeolite-g-PAAM hybrid and PAAM gel samples were accurately weighed (Wo) and put in the stainless steel screen. The samples were extracted with distilled water by using a shaker incubator for 24 h at 80 °C. After extraction, the samples were removed and dried in a vacuum oven at 60 °C to a constant weight (Wi) to determine the insoluble fraction in the samples gravimetrically.

The Gel Fraction (%) was calculated by the following equation:

\[ \text{Gel Fraction (\%) = } \frac{W_f}{W_o} \times 100\% \]  

Where:
Wo= initial weight of PAAM before washing (g)
Wf= final weight of PAAM after washing (g)

Whereas the degree of grafting (%) was calculated by the following equation:

\[ \text{Grafting (\%) = } \frac{W_{i}-W_o}{W_o} \times 100\% \]  

Where:
Wo= initial weight of Zeolite before grafting (g)
Wf= final weight of Zeolite-g-PAAM after grafting (g)

The characterizations of samples were performed by using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Scanning Electron Microscopes (SEM).

2.3. Characterizations

2.3.1. Fourier Transformed Infrared Spectroscopy. Fourier transform infrared spectroscopy (FTIR) was performed on the FTIR spectrometer (IR Prestige-21 Shimadzu, Japan), and the spectra were obtained between 4000 and 400 cm⁻¹. The sample was dispersed in dry KBr.

2.3.2. Thermogravimetric/Differential Thermal Analysis (TG/DT) Analysis. The thermal analysis was carried out using DTG-60 Shimadzu TA-60 WS 2301. 10 mg sample was put on an aluminum holder and heating up to 600 °C for one hour.
2.3.3. **Scanning Electron Microscope (SEM).** The morphologies of the samples were inspected using scanning electron microscopy (JEOL-JSM-6510LV) with several magnifications.

3. Results and discussion

Figure 1 shows that gel fractions increase with the increased of irradiation doses and the highest gel fraction of 99.86% of PAAM was reached at 25 kGy of irradiation dose. As shown in Figure 2, this result complied with the result of the degree of grafting of PAAM onto zeolite that achieved at the same dose level. Figure 2 also reveals that the highest degree of grafting of 48.05%, was obtained at the highest monomer concentration. The degree of grafting then tends to decrease as the irradiation dose increase up to 75 kGy.

![Figure 1](image1.png)

**Figure 1.** Effect of irradiation dose on gel fraction of PAAM.

![Figure 2](image2.png)

**Figure 2.** Effect of irradiation dose on the degree of grafting of zeolite-g-PAAM.
According to the Kickelbick [10] as proposed in Figure 3, there are two possible pathways of the grafting mechanism to porous material such as zeolites which are (i) direct threading of preformed polymer through the host channels (soluble and melting polymers) which is usually limited by the size, conformation, and diffusion behavior of the polymers named “grafting to”, and (ii) the in situ polymerization in the pores and channels of the hosts named “grafting from”. Puspitasari et al. [11] has observed the ESR spectra of zeolite before and after γ-irradiation, which revealed two prominent peaks with g-values of 1.99 and 1.95 indicating the presence of oxygen structure vibration of non-bridging oxygen hole centers (≡Si–O•) and dangling bonds (≡Si•) as anticipated by Catlow et al. [12].

Figure 3. The possible pathway of grafting mechanism of polymer onto 3D porous inorganic material [10].

As reported by Zhang et al. [13], the radiolytic events in zeolites can be expressed by a sequence of reactions as described below:

\[ Z \rightarrow h^+ + e^- \quad \text{(ionization of zeolite frameworks)} \] (3)
\[ h^+ + e^- \rightarrow \text{recombine (electron – hole recombination)} \] (4)
\[ h^+ \rightarrow h_{\text{trap}}^+ \quad \text{(hole trapping)} \] (5)
\[ e^- \rightarrow e_{\text{trap}}^- \quad \text{(electron trapping)} \] (6)
\[ h_{\text{trap}}^+ + e_{\text{trap}}^- \rightarrow \text{recombine (trapped charge recombination)} \] (7)
\[ e_{\text{trap}}^- + Q \rightarrow Q^- \quad \text{(quenching of trapped electrons)} \] (8)

This result was suggesting that the grafted polyacrylamides may be chemically bound to the zeolite frameworks as well as polyacrylonitrile (PAN).

The FTIR spectra of zeolite (green line), PAAM (black line) and zeolite-g-PAAM hybrid (red line) are presented in Figure 4. The characteristic absorption bands of zeolites are –OH (at 3616 cm\(^{-1}\)), T-O of TO\(_4\) tetrahedral (at 1060 cm\(^{-1}\)) and O–T–O symmetrical stretching (at 794 cm\(^{-1}\)), another peak at 1629 cm\(^{-1}\) reveals the association between water molecules with Na or Ca atom inside zeolite porous which indicating hydration of zeolites. The characteristic bands of PAAM were observed at 3435 cm\(^{-1}\) of NH\(_2\) stretching, at 1640 cm\(^{-1}\) of amide (C=O stretching and N-H bending) and C-N stretching at 1425 cm\(^{-1}\) [6,14]. The FTIR spectra of the hybrid reveal that all peaks appeared in zeolite and PAAM also present in the Zeolite-g-PAAM hybrid which means the copolymerization process successfully occurred.
The thermal stability of the polyacrylamide and hybrid was investigated by thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA). Figure 5 presents the thermogram of Zeolite, PAAM and Zeolite-g-PAAM hybrid. It was shown that after heating up to 600 °C the weight loss of zeolite reduces to 8.80%. It was found that the weight loss of the zeolite was the lowest, whereas the weight loss of PAAM was the highest compared to that of Zeolite-g-PAAM hybrid. The weight loss values of PAAM and Zeolite-g-PAAM hybrid were 80.94% and 19.02% consecutively. The result shows that the thermal properties of the PAAM in hybrid was much improved by zeolites. The DTA analysis reveals that phase transitions in Zeolite occurred in the high temperature of 555.79 °C, however the phase transition of PAAM and Zeolite-g-PAAM hybrid were obtained at 244.37 °C and 216.54 °C respectively. The result indicates that on heating the PAAM to 244.37 °C, ammonia was liberated, corresponding to the thermal degradation of the organic matter [5, 15,16].

Figure 4. FTIR spectra of zeolite, polyacrylamide and zeolite-g-polyacrylamide.
Figure 5. Thermogram of TG/DT analysis of zeolites, PAAM and zeolite-PAAM hybrid.

The SEM images of PAAM (a) and Zeolite-g-PAAM hybrid (b) presented in Figure 6. It can be seen obviously the difference between PAAM and Zeolite-g-PAAM hybrid. According to Kim et al. [17], the PAAM has pores that can be used to retain water as shown in Figure 6. As it was mentioned in Kicklebick [10], during in situ polymerization on the zeolite, the monomer of acrylamide entered the zeolite pores and grafted along the channel.
Figure 6. SEM Images with the magnification of $75\times$ of Polyacrylamide (a); Zeolite-Polyacrylamide (b) and with the magnification of $200\times$ of Polyacrylamide (c); Zeolite-Polyacrylamides (d).

4. Conclusion
The hybrid of Zeolite-g-PAAM is successfully obtained by simultaneous gamma radiation-induced grafting copolymerization technique. The optimum dose is 25 kGy with the degree of grafting is 48.01%. The FTIR characterization confirms that functional groups of PAAM have attached to the zeolite. Moreover, the TG/DT Analysis shows that the thermal stability of the hybrid is improved by zeolite. Furthermore, The SEM images reveal that the surface morphology of the Zeolite-g-PAAM hybrid completely different from the PAAM.

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