Changes in the structure, crystallinity, morphology and adsorption property of gamma-irradiated Philippine natural zeolites

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Abstract

Gamma-irradiation of raw, Na-exchanged, NaOH-, and HCl-modified Philippine natural zeolites (PNZ) have been performed at different irradiation doses. XRD, FTIR, and SEM were used to observe the changes in the structure, crystallinity, and morphology of the zeolite samples. The exposure to γ-rays causes varying effects for raw and chemically modified zeolites with non-linear dependence on the irradiation dose. Irradiation results in a general reduction of unit cell volumes of the component zeolites. At low γ-irradiation dose (≤ 400 kGy), raw and NaOH-modified zeolites, experience an improvement in the crystallinity. Higher irradiation dose (700 kGy) leads to structural degradation. In contrast, the crystallinity of HCl-modified zeolites slightly diminishes at a lower dose but improves at a higher dose. On one hand, the exposure to γ-radiation at a dose level of 400 kGy generally degrades the crystal structure of Na-exchanged raw zeolites. Further, adsorption experiments were conducted to investigate how γ-radiation affects the Cu²⁺ sorption property of zeolites for possible applications in heavy metal decontamination in the semiconductor industry.

1. Introduction

Zeolites refer to a group of soft, porous and hydrated aluminosilicates of tectosilicate type made of interconnected tetrahedra composed mostly of aluminum (Al), silicon (Si) and oxygen (O) atoms. They have a very high internal surface area due to their unique open, honeycomb-like framework structure which is basically made up of [AlO₄]³⁻ and [SiO₄]⁴⁻ tetrahedra interconnected through the oxygen atoms located at the corners [1]. When Si is substituted by Al in the zeolite framework, it results in a negatively charged structure that is neutralized often by some alkali and/or alkaline earth cations such as Na⁺, K⁺, Ca²⁺, and Mg²⁺ [2]. These cations are mobile and could be easily exchanged with other cations in a solution, depending on their size and charge density [3], giving the zeolites its capability to absorbed cations and positively-charged polyatomic ions.

Natural zeolites have been extensively studied for heavy metal and radionuclides sorption [4–8]. It can be a good adsorbent for heavy metals depending on its base zeolite components and amount of impurities. To enhance the adsorption, zeolites are modified through various means. Chemical modification using acidic and basic solutions are typically employed to minimize impurity content or to change the Si/Al ratio of the base zeolite components [9, 10]. Ion-exchange is normally done to remove cations initially adsorbed by zeolite providing additional sites for cation capture [5, 9, 11]. Others employ plasma modification to increase the adsorption uptake and surface roughness or reduce metal ions inside the zeolite structure [5, 12–16]. Modification using ionizing radiation has been studied long ago but there were only a few reports regarding this technique at present [17–21]. Irradiation induces structural radiation defects with controllable concentration
2.1. Philippine natural zeolite

In a recent report, the exposure of natural zeolites to 8 MeV electrons helped in reducing the activity of liquid nuclear waste through the adsorption of nuclear radioisotopes $^{137}$Cs, $^{134}$Cs and $^{60}$Co [21]. Electron irradiation causes the displacement of water, as an intact molecule, by either direct collision or as constituent fragments, in the form of separate ions and radicals, by radiolysis. The displacement of water that originally resides in the zeolite cages and the changes in the charge-states of sub-lattices may provide sites for the capture of radioactive Cs$^+$ and other cations.

Thermally activated (550 °C) NdX and NdY zeolites irradiated with 1.5 and 10.0 Mrad $\gamma$-rays exhibited higher catalytic activities in the cracking of cumene than unirradiated ones according to a study [18]. Higher irradiation doses resulted in more active dehydrated zeolites than those irradiated with a lower dose. The higher activity was attributed to the formation of tricoordinate aluminum atoms in the zeolite framework, which lead to an increase of acidic sites. On the other hand, irradiated hydrated (not heated) NdX and NdY zeolites showed lower catalytic activity.

However, there was a report that electron irradiation significantly decreases the sorption capacity of tritiated water (HTO) [19]. The sorption apparently decreases as irradiation dose is increased from $3 \times 10^{10}$ to $10^{17} \text{e}/\text{cm}^2$, which was attributed to the destruction or amorphization of the zeolite framework under high dose irradiation. Meanwhile, gamma irradiation of zeolites that was heated at 700 °C displayed a slightly enhanced HTO sorption.

There was also another study that reports a decrease in the ion exchange capacity for Cs$^+$ and Sr$^{2+}$ of e-irradiated (10$^{-2}$ to 10$^{-5}$ e/\text{cm}^2) clinoptilolite for both untreated and cation-exchanged samples [20]. Likewise, $\gamma$-irradiation at 200 and 700 kGy also resulted in a decrease in the sorption uptake for the two radionuclides.

In another study, the effect of $\gamma$- and (n, $\gamma$)-irradiation on the adsorption, catalytic properties and the structure of zeolite NaA was studied [23]. It was found that a non-linear dependence of adsorption and catalytic properties on the irradiation dose in the range of 0–120 Mrad at any temperature was detected. It was also established that the irradiation resulted in the radiolysis of structural OH-groups, creating active centers of different stability and caused structural changes.

The effects of ionizing radiation in the adsorption and catalytic behavior of zeolites could be explained by the changes in the structure and crystallinity of the material and the formation of electrically charged defects (i.e. vacancies, point defects, radiation damage centers) which may provide positive or adverse effects. The present study aims to investigate the changes in the structure, crystallinity, and morphology of raw and chemically modified Philippine natural zeolites irradiated with gamma-rays at varying absorbed doses. Further, the Ca$^{2+}$ sorption uptake will be investigated to determine if gamma-irradiation is a viable method to enhance the adsorption property of the zeolites. This research further aims to be applied in the heavy metal decontamination of industrial wastes from the semiconductor industries in the Philippines.

2. Materials and methodology

2.1. Philippine natural zeolite (PNZ)

The Philippine natural zeolite used in this study was supplied by SAILE Industries Inc. It was mined from Mangatarem, Pangasinan in the northern region of Luzon, Philippines. The chemical composition of the particular batch of Philippine natural zeolite (PNZ) used in this study, based on various chemical analysis, is shown in table 1. The data was provided by the supplier. The main components include silica and alumina amounting to 55.29% and 12.63% of the total weight respectively. It also contains iron oxide, magnesia, lime, soda, and potash. The sample contains a significant amount of moisture (7.04%) and volatile compounds (14.71%) which is perhaps attributed to the organic matter content of the material. The material contains approximately 67.92% of dehydrated zeolite based on the amount of silica and alumina. The cation exchange capacities (CEC) of the raw zeolite were equal to 128.06 and 51.45 meq/100 g as measured using ammonium acetate and barium acetate methods respectively based on chemical analysis report given by the supplier.

2.2. Pre-treatment and gamma-irradiation of PNZ

The Philippine natural zeolite (PNZ) was pre-conditioned using basic and acidic solutions as this method is commonly employed in the laboratory and in the industry as a means to remove impurities and/or enhance the adsorption/catalytic property of the natural zeolites. Firstly, 1.5 M NaOH solution was prepared using NaOH pellet (Merck, 99%). The concentration was chosen as it was found to be the optimum concentration in modifying the zeolites using NaOH solution according to a study [10]. For every 250 ml of the NaOH solution, 25 g of PNZ was added and soaked for 6 h. It was washed with 0.5 l of deionized (DI) water three times and soaked for 24 h in 250 ml of 4.0 M NaCl solution (Mallinckrodt, analytical reagent). The adsorbent was washed...
with 0.5 l of DI water three times. On the final wash, drops of 1 M HCl solution were added to bring the pH to a neutral level. The adsorbent was collected and oven-dried at 150 °C for 5 h. The sample was re-pulverized for 20 min using an agate mortar and pestle.

Likewise, a 3.8 M HCl solution (Merck, fuming 37%) was prepared. For every 250 ml of HCl solution, 25 g of PNZ was added and soaked for 6 h. It was washed with 0.5 l of DI water three times and soaked in 250 ml 4.0 M NaCl solution for 24 h. Again, the PNZ was washed three times with 0.5 l of DI water. On the final wash, drops of 1 M NaOH solution were added to bring the pH to neutral. The adsorbent was collected and oven-dried at 150 °C for 5 h. The sample was re-pulverized.

Additionally, another sample was prepared by soaking the raw PNZ with 4.0 M NaCl solution for 24 h. The Na-exchanged zeolite was rinsed, oven-dried and regrind like the other samples.

The untreated, Na-exchanged, HCl-treated and NaOH-modified PNZ were gamma-irradiated at varying dose rate using the 60Co source of the Multipurpose Irradiation Facility of the Philippine Nuclear Research Institute until the samples have accumulated an absorbed dose of 200, 400 and 700 kGy. Due to the high dose required by the samples (contained in sealed PET tubes, 2.7 cm diameter, 8.5 cm height), it was positioned closest to the source to get the highest possible dose rate. Ethanol chlorobenzene (ECB) dosimeters which are traceable to the National Physical Laboratory (NPL) of the United Kingdom were used to measure the absorbed dose and for process control. ECB dosimeter was measured using Oscillotitrator Radelkis OK-302/1. Table 2 shows a summary of the actual dose absorbed by the samples produced for this study.

### 2.3. Characterizations

The untreated, modified and gamma-irradiated zeolites were analyzed with an x-ray diffractometer (SHIMADZU, XRD-7000 Maxima) using Cu Kα (1.5406 Å) radiation to check their crystallinity and structure. The continuous scan was conducted with a speed of 2.00° min⁻¹ from a range of 2θ = 0°–40°. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) analyzer (Perkin Elmer FT-IR Spectrometer) and scanning electron microscope (SEM SU1510, Hitachi High Technologies, Japan) were used to examine the changes in the vibrational groups present in the samples and observe their morphology, respectively.

### 2.4. Batch adsorption tests and analytical technique

The adsorption uptake of the samples was assessed through adsorption experiments. Stock solution with a concentration of 1000 mg Cu²⁺/L was firstly prepared by dissolving 2.60 g of copper sulfate pentahydrate [CuSO₄·5H₂O, Unilab, 95.8%] with 1.00 l DI water.

In every experiment, a feed solution with 100 mg Cu²⁺/L concentration is prepared from the stock solution. For every 100 ml of the feed solution, 0.25 g of adsorbent was added. The mixture was agitated using a batch shaker (GFH 3020) at 125 rpm under ambient temperature for 5 h. The adsorbent was separated from the supernatant using a centrifuge (HSIANGTAI) (duration, 5 min; speed, 5) and a Nylon syringe filter (0.45 μm pore size, 25 mm diameter).

The concentration of Cu²⁺ in the supernatant solution was measured using SHIMADZU AA-7000 Atomic Absorption Spectrometer. The AAS was firstly calibrated before using by measuring standard solutions to produce a suitable calibration curve ($R^2 \geq 0.996$).
The adsorbed ions per gram of the sorbent are evaluated using the equation

\[ q = \frac{(C_0 - C_i)V}{m} \]  

where \( C_0 \) is the initial concentration of ions (mg Cu\(^{2+}\)/L), \( C_i \) is the concentration (mg Cu\(^{2+}\)/L) of the supernatant after some time \( i \), \( V \) is the batch volume (L) and \( m \) is the mass (g) of the adsorbent.

### 3. Results and discussion

#### 3.1. Structure and crystallinity of raw and chemically modified PNZ

Figure 1 shows the x-ray diffractogram of the raw Philippine natural zeolite (PNZ). The peaks were attributed mostly to clinoptilolite- [24] and mordenite type [25] zeolites and Ca-montmorillonite [26] which are the main components of the PNZ. Peaks from (0 1 1)/ (1 0 1), (0 1 2)/ (1 0 2) and (2 0 0) planes of quartz [27] were also identified. The results coincide well with the reported composition of the material based on previous works [6, 28–34].
Figure 2 shows the XRD patterns of the raw and chemically modified Philippine natural zeolites at a different angle range of 2θ: (a) 3°–40° and (b) 21°–24°.

Figure 2 shows the XRD patterns of the raw zeolite together with the NaCl–, NaOH– and HCl-modified zeolites. As compared to the raw zeolite, the Na-exchanged PNZ contains several peaks that are slightly shifted to the left. This is most apparent at the highest peak around 2θ = 22.5° which corresponds to that of clinoptilolite. This means that the lattice parameters of the component zeolites increased in value which is perhaps due to the incorporation of Na in the zeolite framework after the ion-exchange. It can be observed that the peak at 2θ = 5.48° attributed to the (001) plane of the montmorillonite disappeared. The montmorillonite might have been washed or destroyed upon heating at 150 °C resulting in the appearance of a broad peak at around 2θ = 6.78° which is perhaps attributed to amorphous siliceous material.

For the NaOH-modified zeolites, again, several peaks slightly shifted to the left indicating an increase in the lattice parameters which is due to the incorporation of Na in the zeolite frameworks. Take note that the sample was also subjected to Na-exchange. The highest peak of the Na-exchanged zeolite has narrower width compared to the highest peak of the raw zeolite signifying better crystallinity brought by partial dissolution of amorphous siliceous materials. However, it has a lower intensity which means that some crystalline zeolites underwent desilication.

On the other hand, the immersion of the PNZ to HCl solution caused shifting of peaks to the right which suggests that the lattice parameters had decreased. Moreover, almost all peaks have broadened, which is clearly observed at the highest peak, implying a significant non-uniform lattice distortion. HCl modification moderately alters the structure of the zeolite. Typically, the immersion of the material to acidic solutions causes dealumination [35] and/or leaching of metallic components of the material. In this case, the Al atoms in the zeolite frameworks have been removed which resulted in the shrinking of affected unit cells. The removal of Al atoms also resulted in structural damage in the zeolite frameworks which lead to a poorer crystallinity as also implied by the elevated background noise in the XRD pattern of HCl-modified zeolite. Crystalline zeolites have decreased as implied by the lower intensity of the highest peak compared to that of the raw zeolite.

3.2. Effects of gamma irradiation in the structure and crystallinity

Meanwhile, the effects of gamma irradiation in the x-ray diffractograms of the zeolite samples are shown in figure 3. A notable peak shifting to the right was observed in the raw zeolite, as can be observed in figure 3(a), which is most apparent in the highest peak at around 2θ = 22.42°. This implies contraction of the unit cell volume in the structure of the component zeolites. The cause might be attributed to the elimination or knocking-off of water residing in the zeolite micropores as was observed in a previous study [21]. The peaks are more intense which implies better crystallinity.

From the diffractograms of the Na-exchanged samples in figure 3(b), all the irradiated samples have peaks that are also shifted to the right which again suggests shrinking of the unit cells due to possible displacement of water molecules in the zeolite micropores. The width of the peaks is practically the same as that of the unirradiated Na-exchanged zeolite. However, the Bragg peaks were generally more intense compared to the unirradiated sample. This implies bigger crystallite size which might be attributed to a more crystalline structure. But further irradiation at 700 kGy caused the peak corresponding to amorphous siliceous materials at around 2θ = 6.62° to become very broad which indicates significant damage in the crystal lattice.

For the HCl-modified zeolite, gamma-irradiation at 400 kGy barely caused peak shifting, although some peaks experienced a slight shift to the right which indicates that some of the lattice parameters of certain zeolite
Figure 3. Comparison of the XRD patterns of the unirradiated and γ-irradiated (a) raw, (b) Na-exchanged, (c) HCl- and (d) NaOH-modified Philippine natural zeolites.
component/s have been reduced to some extent. The peaks became less intense in general suggesting an inferior crystallinity at this dose level.

The changes in the XRD patterns of the gamma-irradiated NaOH-modified zeolites are shown in figure 3(d). At 200 kGy, the highest peak shifted to the right, with an increase in the intensity, which means that aside from contraction of unit cells due to the removal of water in the zeolite framework, the material became more crystalline. Irradiation at 400 kGy made the peak shifted further towards the right. Additionally, it made the peak narrower, which indicates that the sample has gained better crystallinity than the sample irradiated at 200 kGy. However, after obtaining 700 kGy absorbed dose, the intensity of the highest peak has been reduced. Further, it was observed that the peak width has widened, as well as the width of the peak corresponding to the amorphous siliceous material at $2\theta = 6.56^\circ$. These imply a remarkable degradation of the crystallinity at this irradiation dose level.

At a low dose ($\leq 400$ kGy), gamma-irradiation could improve the crystallinity. However, a higher dose might be detrimental to the structure of the material. This same trend was also observed in a previous study [23], wherein an ordering of crystal lattice structure of NaA zeolite was detected at small doses (0.5–5 Mrad) of $\gamma$- and $n$-radiation while a disordering was obtained at higher doses. Accordingly, the ordering of crystal structure was brought by the annihilation of initial or biologic defects while the disordering is the result of the accumulation of radiation defects. Perhaps, this also explains the changes in the crystal structure of the $\gamma$-irradiated NaOH-modified zeolite.

### 3.3. Vibrational groups of raw and chemically modified PNZ

Figure 4 shows the IR transmittance spectra of the unirradiated samples which include that of raw, NaCl-, NaOH- and HCl-modified zeolites. The vibration bands present in each sample are summarized in table 3. For the raw zeolites, the band at 3620 cm$^{-1}$ corresponds to the O–H stretching of inter-porous water [36]. Symmetric and asymmetric stretching of hydroxyl functional groups are found at wavenumbers 3387, 2989, 2909 and perhaps, 2660 cm$^{-1}$ [37]. The usual bending of H$_2$O molecules attached to the zeolite surface is found at 1630 cm$^{-1}$ [36, 38]. Asymmetrical stretching of internal tetrahedra (O–Si–O and O–Al–O) are observed at 1205, 1008, 915 and probably, 880 cm$^{-1}$ [36]. The vibration band at 790 cm$^{-1}$ is attributed to the symmetrical stretching of external linkages while the bands at 790 and 688 cm$^{-1}$ are brought by the symmetrical stretching of internal tetrahedra.

Some of the vibration bands shifted to some degree for the chemically modified samples. Notably, the bands at 2989 and 2902 cm$^{-1}$ corresponding to the symmetric and asymmetric stretching of hydroxyl groups do not exist in the Na-exchanged zeolites.

### 3.4. Effects of gamma-irradiation in the vibrational groups of raw and chemically modified PNZ

Figure 5 presents the changes in the intensities of selected vibration bands of the different samples as a function of irradiation dose. There is no general trend in the IR spectra of the $\gamma$-irradiated raw zeolites. For the sample irradiated at 200 kGy, there was a minimal change in the intensities of major vibrational groups. Note that a lower IR transmittance means a higher intensity of the vibration band which implies a larger surface area [39] or can also mean a larger amount of the material that causes such vibration. However, after achieving a 400 kGy absorbed dose, the intensity of the bands corresponding to the bending of water molecules and the symmetric and/or asymmetric vibration of hydroxyl groups remarkably increased which suggests that the material...
Table 3. Vibration bands present in the IR transmittance spectra of raw and chemically modified zeolites.

| Vibration bands                                      | Raw Zeolite (cm⁻¹) | NaCl-Zeolite (cm⁻¹) | NaOH-Zeolite (cm⁻¹) | HCl-Zeolite (cm⁻¹) |
|------------------------------------------------------|--------------------|---------------------|---------------------|-------------------|
| O–H stretching of the inter-porous H₂O              | 3620               | 3620                | 3628                | 3623              |
| Symmetric and asymmetric stretching vibration of     | 3387               | 3411                | 3400                | 3400              |
| hydroxyl functional group                             |                    |                     |                     |                   |
|                                                      | 2989               | —                   | 2989                | 2988              |
|                                                      | 2902               | —                   | 2902                | 2902              |
|                                                      | 2660               | 2652                | 2660                | 2655              |
| Bending of H₂O molecules attached to the zeolite     | 1630               | 1632                | 1630                | 1630              |
| surface                                             |                    |                     |                     |                   |
| Asymmetric stretching of internal tetrahedra (O–Si– | 1205               | 1200                | 1200                | 1200              |
| O and O–Al–O)                                        | 1008               | 1008                | 1006                | 1020              |
|                                                      | 915                | 917                 | 917                 | 915               |
|                                                      | 880                | 880                 | 883                 | 883               |
| Symmetric stretching of external linkages            | 790                | 792                 | 791                 | 792               |
| Symmetric stretching of internal tetrahedra          | 688                | 692                 | 694                 | 694               |
|                                                      | 664                | 664                 | 663                 | 663               |

adsorbed more moisture. These water molecules are not necessarily found inside the zeolite micropores, as the zeolite structures have contracted according to XRD which means that these waters are located at the surface of the zeolite. Additionally, the intensity of the symmetric stretching of external linkages and asymmetric stretching of internal tetrahedra increased implying a better crystallinity of the sample compared to the unirradiated zeolites. Further irradiation caused a decrease in the intensity of these bands. The lowering of the intensities of the bending vibration of water and the vibrations of OH-groups might indicate radiolysis while the decrease in the intensity of the O–Si–O and O–Al–O stretching of external and internal tetrahedra indicates the breaking of these bonds. These phenomena were also observed in a previous study on zeolite NaA [23]. The production of hydroxyl radicals and hydrated protons [H⁺(H₂O)ₖ⁺], as a consequence of radiolysis, might be able to break Si–O–Si or Si–O–Al bonds in the zeolite framework [40].

Na-exchanged samples show a decrease in the intensity of the vibration of water residing at the zeolites’ micropores after irradiation with 200 and 400 kGy absorbed dose but got an increase at 700 kGy. The same trend has been observed with the vibration groups related to the stretching of internal tetrahedra. However, the vibration of the symmetric stretching of external linkages experienced a continuous minor decrease in the intensity. Generally, gamma-irradiation leads to the degradation of the crystal structure of Na-exchanged zeolites.

For the HCl-modified zeolites, there was a decrease in water content after gamma-irradiation. The (O–Si–O and O–Al–O) symmetric stretching of internal tetrahedra experienced a decrease in the intensity at a lower dose (≤ 400 kGy) suggesting a disturbed crystal structure. This agrees well with XRD results which show that the material is less crystalline at 400 kGy. Further, IR results show that the (O–Si–O and O–Al–O) symmetric stretching got an increase at higher dose (700 kGy) which means that the material underwent enhancement of crystallinity which does not necessarily mean an improvement in the crystal structure of component zeolites. It is because gamma-irradiation leads to the recrystallization and/or formation of other tectosilicates as implied by the red shifting of the vibration band corresponding to the symmetric stretching of O–Si–O and O–Al–O. As observed in the FTIR spectra which are not shown in this paper, which might not necessarily zeolites. This is further proven by a significant leap in the intensity of symmetric stretching of external linkages located at 792 cm⁻¹ which also suggests that the crystallized material is not of zeolitic type.

For the NaOH-modified zeolites, the intensities of the vibration corresponding to water and hydroxyl functional group decrease a little at 200 kGy and 400 kGy. The water molecules and hydroxyl molecules have been ‘knock-off’ by gamma-radiation. Water was further removed at 700 kGy absorbed dose. A remarkable trend was observed for the band corresponding to the asymmetric (O–Si–O and O–Al–O) stretching of internal tetrahedra. After obtaining a dose of 200 kGy, the intensity increased signifying a better crystallinity. A slight improvement in the intensity was recorded at 400 kGy. But upon further irradiation, the intensity decreased significantly. The effects of gamma irradiation, aside from the removal of water from the zeolites’ micropores, could improve the crystallinity of the material at low doses, which is ≤ 400 kGy in our case. Perhaps, crystal defects are corrected, filling-up the vacancies and realigning interstitial point defects. However, at higher doses, greater than 400 kGy, more and more O–Si–O and O–Al–O bonds break leading to the deterioration of the crystallinity. This trend was almost like that of gamma-irradiated raw zeolites but is exactly opposite to what happened to the HCl-treated zeolites.
Gamma-rays interact differently on dissimilar materials. The total attenuation coefficient could predict the level of interaction of \( \gamma \)-rays in each material. Table 4 provides the total attenuation coefficients considering a coherent scattering of the component materials of PNZ with regards to the energies of the \( \gamma \)-rays produced by \(^{60}\)Co (1.173 and 1.332 MeV).\(^{55}\) The values were computed using XCOM, the online attenuation coefficient calculator of the National Institute of Standards and Technology (NIST) \(\text{https://physics.nist.gov/PhysRefData/Xcom/html/xcom1.html}\). Water has the highest value which means that gamma-radiation affects it the most.

Figure 5. Variation in the intensities of selected vibration bands in response to the absorbed dose of the (a) raw, (b) NaCl-exchanged, (c) HCl-modified, and (d) NaOH-modified Philippine natural zeolites.
followed by montmorillonite, clinoptilolite, chabazite, and mordenite. Quartz is least affected. It is no wonder why water and hydroxyl groups undergo radiolysis more easily, which is indeed observed in each sample at all irradiation doses considered. Due to the lower attenuation coefficients of the aluminosilicates, they are less affected at low irradiation dose. However, the radicals and hydrated protons formed from radiolysis could damage the crystal structures of the aluminosilicates. The growing number of radicals and the accumulation of damaged unit cells directly destroyed by γ-rays result in the amorphization of the material at higher irradiation doses.

3.5. Morphology

The SEM micrographs of the raw and γ-irradiated Philippine natural zeolites with 400 kGy absorbed dose are shown in figure 6. The raw zeolite powder, as seen in figure 6(a), is made up of particles with irregular sizes and shapes. The largest particle observed has a length of ~50 μm. The zeolite surface is rough and flaky. In comparison to the γ-irradiated sample in figure 6(e), there was no significant change observed in the zeolite’s surface.

Aside from a clumpier or more aggregated particles, the effects of exchanging Na⁺ ions using NaCl solution brought no remarkable changes in the morphological and topographical characteristics of the zeolite. Effects of gamma-irradiation are hardly figured-out from the SEM micrographs.

Figure 6(c) shows the SEM images of HCl-modified zeolites. Compared with the raw zeolites, the particles of this sample appear to have a significantly greater number of pores and/or cavities after soaking in the acidic solution. The pores appear to penetrate through the interior of the particles which probably increased the porosity of the material. These pores were brought by the leaching of the metal-rich regions of the zeolite. The sample exposed to γ-rays, as seen in figure 6(g), has no distinguishable difference even after irradiating the sample at 400 kGy.

The effects of NaOH modification of the zeolite can be seen in figure 6(d). The zeolite particles appear to be etched resulting in a scaly surface. Cracks were formed on the surfaces that almost split the particles into smaller pieces. These are due to the dissolution of amorphous regions of the zeolite and other siliceous materials constituting the material. The effects of gamma-irradiation, as shown in figure 6(h), were not well illustrated in the SEM images.

3.6. Batch adsorption tests

Figure 7 shows the summary of the adsorbed Cu²⁺ ions of the zeolite samples. Chemical modification using the NaOH solution enhanced the sorption uptake from 33.325 mg Cu²⁺/g to 40.888 mg Cu²⁺/g. On the contrary, acid modification degraded the sorption down to 22.387 mg Cu²⁺/g. The main reason for this is the change in the Si/Al ratio. The Si/Al ratio of the NaOH-modified PNZ is lower compared to the unmodified zeolites due to desilication while the HCl-modified PNZ had increased due to dealumination. \(^7\) Exact values of the atomic % were measured via energy-dispersive x-ray spectroscope (UltraDry EDX Detector, ThermoScientific, Massachusetts, USA). The HCl-modified samples contain a lesser amount of Al as a result of dealumination. Hypothetically, the lower the Al atoms, the lesser the adsorption as the negatively charged tetrahedra responsible for cationic-exchange decreases. In addition, although both the acid- and base-modified zeolites were subjected to Na-exchange for 24 h, the immersion of zeolites in NaOH solution is advantageous as the solution also contains Na⁺ ions. Practically, Na-exchange occurs simultaneously upon purification of the samples, ensuring an enhanced removal of the metal cations initially trapped in the zeolites’ active sites.

The effects of γ-irradiation vary from sample to sample. For the raw and HCl-treated PNZ, almost the same trend has been observed in the sorption uptake as shown in figure 7. Irradiation of up to 200 kGy absorbed dose essentially has no significant effects. However, at an absorbed dose of 400 kGy and higher, the uptake lowered by around 22% and 48% in the raw and HCl-modified zeolites respectively. The adsorption uptake did not vary much after further exposure to 700 kGy. Generally, the exposure to γ-rays of these samples brought adverse effects in the sorption property.

| Material          | Chemical formula | Total attenuation coefficient (cm² g⁻¹) |
|-------------------|------------------|---------------------------------------|
|                   |                  | 1.173 MeV                             |
|                   |                  | 1.332 MeV                             |
| Water             | H₂O              | 6.532 × 10⁻²                         |
|                  |                  | 6.120 × 10⁻²                         |
| Clinoptilolite    | Na₆Al₅Si₃₀O₇₂·20H₂O | 5.943 × 10⁻²                     |
|                  |                  | 5.570 × 10⁻²                         |
| Mordenite         | Ca₆Al₃Si₆O₁₈·7H₂O | 6.016 × 10⁻²                         |
|                  |                  | 5.639 × 10⁻²                         |
| Chabazite         | Ca₃(Al₂Si₄O₁₂)·12H₂O | 5.999 × 10⁻²                     |
|                  |                  | 5.622 × 10⁻²                         |
| Montmorillonite   | Ca₆Si₅Al₂Si₄O₁₆·3OH_2·nH₂O | 6.127 × 10⁻²                 |
|                  |                  | 5.742 × 10⁻²                         |
| Quartz            | SiO₂             | 5.880 × 10⁻²                         |
|                  |                  | 5.511 × 10⁻²                         |

\(^a\) for n = 12.
Figure 6. SEM images of the unirradiated (a) raw, (b) Na-exchanged, (c) HCl-modified, and (d) NaOH-modified zeolites and the gamma-irradiated (e) raw, (f) Na-exchanged, (g) HCl-modified, and (h) NaOH-modified zeolites at 400 kGy absorbed dose.

Figure 7. Summary of the adsorption uptake of the different samples.
On the other hand, the adsorption of the NaOH-modified zeolite improved by 16.29% after obtaining an absorbed dose of 200 kGy and 25.20 % at 400 kGy. But it decreased a little at 21.36% after attaining a dose of 700 kGy.

Generally, γ-irradiation does not provide positive effects on raw natural zeolites. As a matter of fact, irradiation at 400 kGy dose could even degrade the sorption. A possible explanation is that Na⁺ or other exchangeable cations like Mg²⁺ and Ca²⁺, can be displaced to the locked-in sites (i.e. sodalite cages) of the zeolites upon contraction of the framework and render themselves inaccessible for cation exchange [17]. Likewise, the γ-irradiation of HCl-treated zeolites does not improve the sorption, rather reduced adsorption uptake. Even though the sample is more crystalline based on XRD, γ-irradiation resulted in the recrystallization of tectosilicates that are not necessarily zeolites. This means that γ-irradiation could potentially transform zeolites into impurities which reduces the sorption capacity of the sample. On the contrary, gamma-irradiation improves the adsorption of NaOH-treated zeolites. The removal of various molecular species that were originally contained in the zeolite cage pores, such as water, might provide additional sites for the capture of cations [21]. Unlike in the raw zeolites, where Na⁺ ions are scarce, NaOH-modified zeolites contain a far greater amount of Na⁺ ions. Therefore, it has more than enough to fill in the locked-in and other active sites within the zeolite cages, avoiding the complete closure or collapse of zeolites’ channels which could interfere in the cation exchange. Further, γ-irradiation of NaOH-modified zeolites has a better crystal structure which certainly helped in curbing Cu²⁺ ions in the aqueous solution.

Absorption of gamma photons from the 60Co would result primarily in Compton scattering [17]. Energetic scattered electrons are envisaged to displace mobile cations and to some extent, the framework atoms from their initial positions. Another influence of γ-irradiation is the radiolysis of water which results in the formation of H⁺ and OH⁻ [19]. Since the zeolites’ surface is negatively charged, H⁺ ions could temporarily attach to the active sites, which is then replaced during cation exchange. These phenomena are most likely to occur on NaOH-modified zeolites, which is why the improvement of the sorption uptake is very apparent. On the other hand, the active sites of HCl-treated zeolites are already neutralized upon dealumination due to the hydrolysis of Al–O–Si bonds which resulted in the formation of hydrated silica gel and aluminum salts [19].

4. Conclusion

The exposure to γ-rays causes varying effects for raw and chemically modified zeolites with non-linear dependence on the irradiation dose. The most obvious consequence of gamma-irradiation is the contraction of the zeolite structure due to the removal of water in the zeolite micropores as a result of radiolysis. For the raw and NaOH-modified zeolites, it was observed that low gamma-irradiation dose (≤ 400 kGy) could improve the crystallinity of the zeolite. Higher irradiation dose (700 kGy) leads to structural degradation as the damage caused by γ-rays and radicals produced from the radiolysis of water and hydroxyl groups accumulate. HCl-treated zeolites have diminished its crystallinity at 400 kGy dose but improved at a higher irradiation dose. However, it does not necessarily mean better crystal structure of component zeolites as recrystallization of other tectosilicates have occurred. On one hand, γ-irradiation generally degrades the crystal structure of Na-exchanged zeolites. There are no significant changes in the morphology of all the samples even after obtaining a relatively high dose of γ-irradiation.

Generally, γ-irradiation does not improve the sorption of the raw zeolites. It even degrades the sorption of the zeolite when exposed to γ-rays at doses of 400 and 700 kGy. Similarly, γ-irradiation does not enhance the sorption property of HCl-treated zeolites. It results in further reduction of the sorption uptake because γ-irradiation leads recrystallization of certain tectosilicates which are not necessarily of zeolites based on the IR spectra. However, γ-irradiation improved the adsorption of NaOH-treated zeolites with the optimum sorption observed at a dose of 400 kGy. The removal of various molecular species that were originally contained in the zeolite cage pores, such as water, might provide additional sites for the capture of cations. Unlike in the raw zeolites, where Na⁺ ions are scarce, NaOH-modified zeolites contain a far greater amount of these ions. Therefore, it has more than enough to fill in the locked-in and other active sites within the zeolite cages and its outer surfaces, avoiding the complete closure or collapse of zeolites’ channels which could interfere in cation exchange. The improved crystal structure under γ-irradiation might as well contributed to the enhancement of the sorption uptake. The γ-irradiated NaOH-modified Philippine natural zeolites can be a promising adsorbent for the treatment of industrial waste from the semiconductor industries in the Philippines.

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