Chapter 9

Potential Desalination of Coal Seam Gas Coproduced Water Using Zeolite

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Additional information is available at the end of the chapter

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Abstract

Natural clinoptilolite type zeolite was examined for its potential to treat coal seam gas (CSG) water and remove sodium ions to lower sodium adsorption ratio and reduce pH. The effectiveness of unmodified and modified natural zeolite is due to their regular composition and open porous structure, high exchange capacity, mechanical strength and stability, and consistency in particle size. The effects of acid modification in bringing about changes to the physicochemical properties of clinoptilolite underpin the effectiveness of this material for treatment of CSG saline water. The sodium adsorption capacity of acid-modified zeolite increases up to three times greater than that of the unmodified zeolite. The atomic percentage and binding energies of the chemical elements comprising zeolite are changed significantly following the acid modification. The Si/Al atomic ratio increases with increasing sulfuric acid concentration. Dealumination is the main reason for the increase in the surface charge and cation exchange capacity of clinoptilolite after acid modification. It is due to the increased defects in the crystal structure/lattice, which result in increasing numbers of charge vacancies. Sodium-rich synthetic zeolites 4A and Na─Y after acid modification are also examined by following the dissolution of the first-order fast kinetics and recrystallization processes which can be homogeneous or heterogeneous.

Keywords: CSG, acid treatment, SAR, clinoptilolite, surface potential, XPS

1. Introduction

Zeolite is a cost-effective material that has been investigated for its potential use as adsorbents because of its large volumes of internal space [1–3]. It belongs to the group of natural silicate minerals which have high sorption capacity and selectivity resulting from high porosity and sieving properties. The capability of zeolite to exchange cations is one of their most useful properties as it has been used to remove heavy metals, such as Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+}. Of the natural zeolites, clinoptilolite is regarded as the most useful adsorbent. It is also the most researched of all zeolites. Clinoptilolite has a cage-like structure with pores and channels running through the crystal. The cage consisting of SiO_4 and AlO_4 tetrahedral joined by shared oxygen atoms carries a net negative charge which is balanced by the presence of exchangeable cations—especially calcium, sodium, magnesium, potassium, and iron. These ions can be readily replaced by other cations that can easily interact with the negative zeolite framework, such as heavy metals [4–6] and ammonium ions [7, 8]. Due to its very high cationic exchange capacity, clinoptilolite is a potential adsorbent for removing cations from an aqueous solution, for example, in desalination, drinking water purification [9–14] and processing coal seam gas (CSG) coproduced water [15].

CSG can be considered as conventional natural gas that is adsorbed into coal seams in deep underground [16]. The CSG extraction discharges a large amount of water (several megaliters per day). For example, 12.5 giga litres of CSG water was produced and discharged by CSG industry in Queensland, Australia, in 2007 [17]. However, high salt content of the CSG water can potentially harm the environment. Therefore, it cannot be released directly to land or other water resources. Sodium concentration must be reduced to less than 200 ppm for irrigation. Management of CSG water is an environmental challenge. Desalination but with cost-effective technologies is in demand to allow the CSG water usage for beneficial purposes, including irrigation use [18].

Current CSG water management and treatment technologies include infiltration ponds, shallow or deep aquifer injection, reverse osmosis, ion exchange, and subsurface drip irrigation [16]. Unfortunately, these treatments are either rather time-consuming or very expensive. For example, using reinjection to clean up an aquifer with dissolved volatile organic compounds over an area of 3 km^2 needs around 50 years [18]. In addition, reverse osmosis (RO) is effective in removing dissolved salts but produces a significant amount of brines that also need to be addressed and dealt with high capital costs than most other strategies. The additional effort and costs and high capital costs make it difficult for RO to be a cost-effective management option in a large geographical area where raw water is spread over. Hence, a better way of CSG water treatment is urgently needed.

Sodium adsorption ratio (SAR) is an important parameter to analyses the effective removal of sodium when dealing with CSG water managed irrigation [16]. Being calculated as the ratio of Na^+ to Ca^{2+} and Mg^{2+} in the soil, SAR describes the tendency for Na^+ to be adsorbed at soil ion-exchange sites at the expense of other ions (in this case calcium and magnesium ions). Soils with an excess of Na^+, compared to of Ca^{2+} and Mg^{2+}, remain in a dispersed condition, almost impermeable to rain or irrigation water. In general, the higher the SAR, the less suitable the water is for irrigation. Irrigation using water with high SAR may require soil amendments to prevent long-term damage to the soil.

To increase adsorption capacity, natural zeolites can be modified by sole or combined treatments such as chemical attacks (alkali, acids, and salts of alkaline metals) and heating. Different methods are used to prepare zeolites with specific properties for different applications. For example, acid treatment has been shown to improve the adsorption ability and enlarge the pore system of different synthetic zeolites [19–21]. Acid treatment can dealuminate the zeolite structure by applying protons to attack and weaken Al─O bonds, thereby causing skeletal vacancies and defects. They can enlarge the pore mouth of the zeolite and increase the surface area and adsorption ability. Acid treatment is a simple and economical option for increasing the adsorption capacity of natural zeolites that improve the viability of zeolite on CSG water treatment.

In this regard, the applicability of the water treatment method for CSG water using natural zeolite (to reduce the Na^+ content less than 200 ppm, sodium adsorption ratio (SAR) value between 12 and 25, and pH value is about 7) and improved treatments to increase the adsorption ability of the natural zeolite by acid modification is reviewed in this chapter.

2. The effect of zeolite modification by acids on sodium adsorption ratio of coal seam gas water

2.1. Characterization of zeolite before and after acid treatment

The chemical composition of the zeolite (Zeolite Australia Pty Ltd) is shown in **Table 1**. Zeolite treatment was carried out with different acids (H_2SO_4, HCl, and HAc) at various concentrations (0.001, 0.1, 1, and 2 M) in order to increase the adsorption capacity of the sample. The acid treatment included mixing the natural zeolite sample with acid solutions (1:1 weight ratio) and drying of the washed treated zeolite overnight at 80°C. The adsorption experiments were carried out at 10, 20, and 30% solid ratios (w/w) separately for 6 h using an orbital shaker at 200 rpm at room temperature. Primary exchangeable cations and effective cation exchange capacity (CEC) for the natural zeolite sample are Na^+, Mg^{2+}, Ca^{2+}, and K^+. The total CEC for natural zeolite was about 119 meq/100 g, as for cations released from zeolite sample during NH^{4+} exchange [22]. The CEC of 0.1 M H_2SO_4 acid-modified zeolite was about 300 meq/100 g based on the adsorption calculation.

The analysis by X-ray diffraction (XRD) showed that the main compositions were clinoptilolite and quartz and 0.1 M H_2SO_4 acid modification did not change the phases of the zeolite sample. With increasing concentration of H_2SO_4 from 0 to 2 M, the BET surface area of zeolite samples increased from 9.8 to 15.7 m^2/g. The change was attributed to removing fine particles that can clog the zeolite pores and slow the exchange rates [23–26]. In addition, SEM images showed that the modified zeolite surface contained more cracks and small openings compared to the natural zeolite. These details prove the structural changes on the zeolite surfaces after the acid treatment (**Figure 1**).

Compound	SiO_2	TiO_2	AlO_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	SO_3	Total
Zeolite (%)	68.3	0.2	13.0	1.4	0.1	0.8	2.1	0.6	4.1	0.1	8.8	0.5	100

Table 1. Chemical composition of zeolite [15].

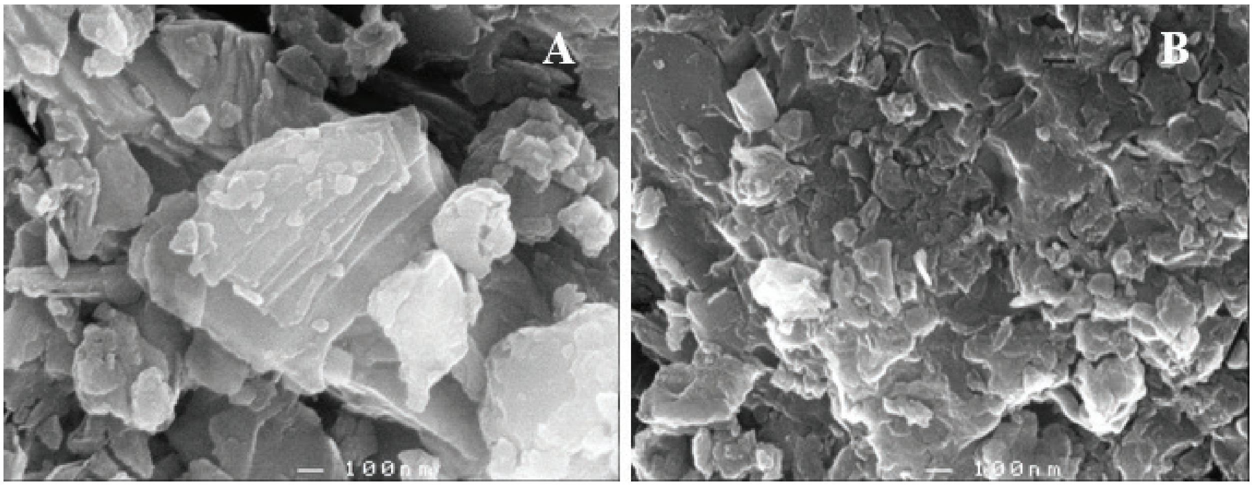


Figure 1. SEM images of (A) natural zeolite and (B) modified zeolite with 0.1 M H_2SO_4 [15].

The DTA/TG tests showed that the natural and acid-modified zeolite samples had the same trend of weight loss. This indicates that both natural and acid-modified zeolite samples have just physically lost moisture content [27]. DTG analysis (**Figure 2**) also showed the surface water desorption decreased with increasing acid concentration at 200°C. Interestingly, for the zeolite modified by 2 M H_2SO_4 solution, the surface water desorption at around 100°C was much reduced. At a higher temperature (350°C), there was no such an evidence of loss of hydrated water occurred with natural and 0.1 M H_2SO_4 acid-modified zeolites. This suggests that acid with high concentration can destroy the pore structure of the zeolite. Particle size analysis showed that the particle size was less than 200 μm, with a mean of about 50 μm.

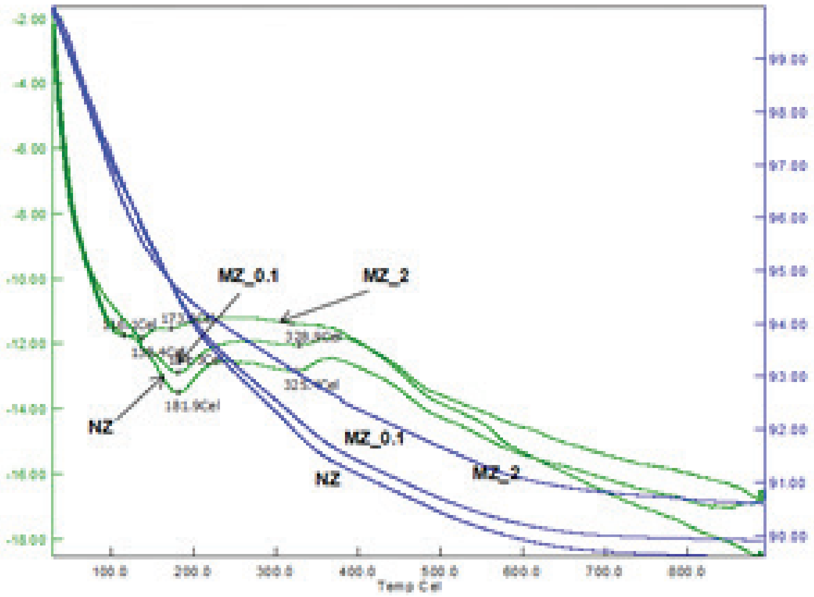


Figure 2. DTA/TG results of the natural and modified zeolite samples with 0.1 M H_2SO_4 (NZ, natural zeolite; MZ_0.1, modified zeolite 0.1 M; MZ_2, modified zeolite 2 M) [15].

The surface potential analysis by electrophoresis (with −38 μm size fractions) was carried out for natural and modified zeolite samples (**Figure 3**). Substitutions of Al^{3+} ions for Si^{4+} in the clinoptilolite lattice and the broken Si—O—Si bonds at the particle surface during the grinding process were the reasons for the surface charge negative [24, 25, 28]. With the pH value changing, H^+ could easily become exchangeable cations. These results agree with the literature data [6, 24]. For each pH value tested, the zeta potential of acid-modified zeolite was always around 9 mV more negative than natural zeolite. It indicates that acid modification weakens the Si—O bond. When there is a cation exchange environment exists, ion exchange can occur easily in acid-modified zeolite surface than natural zeolite.

2.2. CSG water treatment using untreated and acid-treated zeolite

As per the chemical analysis of the CSG water, its pH value is 8.4, SAR 94, concentration Na^+ 563 ppm, Mg^{2+} less than 1 ppm, and Ca^{2+} 2 ppm. SAR is defined as follows:

$$\text{SAR} = \frac{[\text{Na}^+](\text{meq})}{\sqrt{\frac{[\text{Ca}^{2+}](\text{meq}) + [\text{Mg}^{2+}](\text{meq})}{2}}} \tag{1}$$

where $[Na^+]$, $[Ca^{2+}]$, and $[Mg^{2+}]$ are the concentrations in solution and meq is the milliequivalent weight.

The results for Na^+ removal using natural zeolite as a function of solid concentration (weight of zeolite per weight of solution) are shown in **Figure 4A**. A slight decrease in the Na^+ concentration was seen with increasing the solid ratio, while the Mg^{2+} and Ca^{2+} concentrations increased correspondingly. This is the direct result of the ion exchange of sodium with calcium and magnesium which are exchanged and entered the bulk

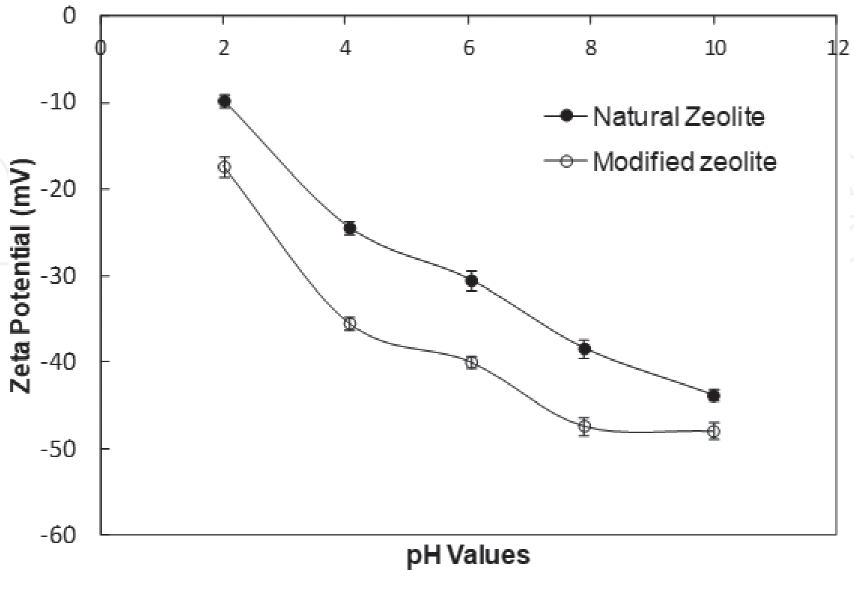


Figure 3. Zeta potential profiles of natural and 0.1 M H_2SO_4 modified zeolite samples [15].

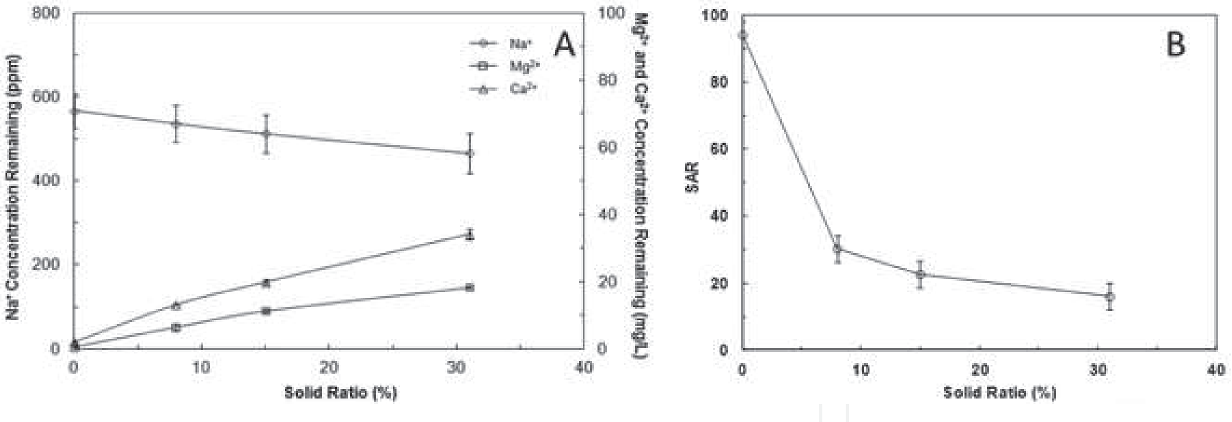


Figure 4. (A) Ion concentrations in CSG water after treatment with natural zeolite. (B) SAR values of CSG water after treatment with natural zeolite [15].

aqueous phase. Because of the decrease in sodium concentration and increase in calcium and magnesium concentrations, the value of SAR decreases with the solid ratio as shown in **Figure 4B**, which is expected. While the SAR value is in the acceptable range between 12 and 25, Na^+ concentration remains high, making the treated water unacceptable for practical purposes.

Figure 5 (left panel) shows the effect of acid modification of zeolite particles on the adsorption of Na^+ ions. The tests were conducted with different concentrations of H_2SO_4 to establish the most suitable acid concentration. The adsorption tests were carried out using an orbital shaker at 200 rpm at the solid ratio of 30% for 6 h. The Na^+ concentration of the CSG water after treatment with the modified zeolite decreases with the increasing acid concentration: The Na^+ adsorption capacity of zeolite can be significantly improved by acid modification. The SAR values with the modified zeolite were slightly higher than natural zeolite due to the release of Mg^{2+} and Ca^{2+} ions during the washing and acid modification process and sequentially lessening Mg^{2+} and

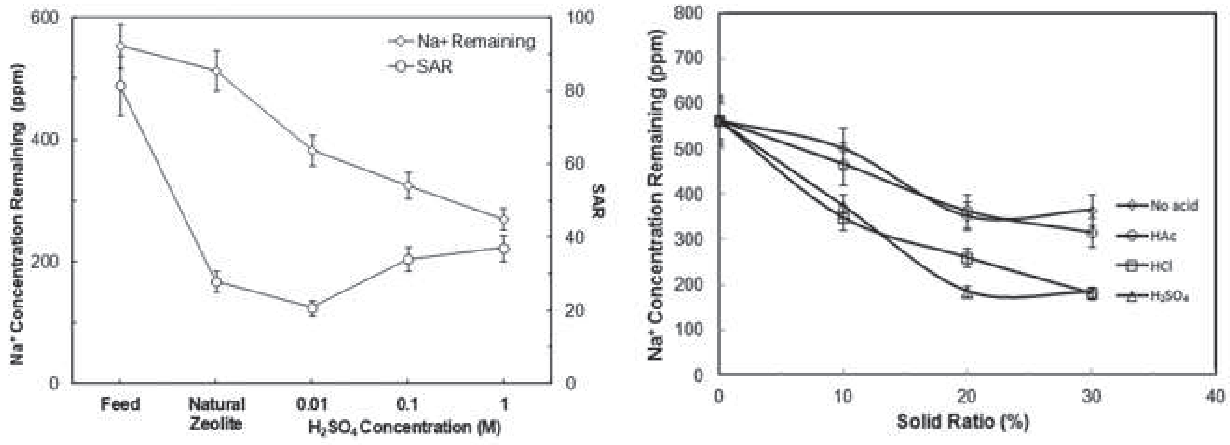


Figure 5. Left: Na^+ concentration and SAR in CSG water after treatment with 30% solid ratio zeolite (natural and modified by H_2SO_4) [15]. Right: Na^+ removal by the modified zeolite as a function of acid type and solid concentration at room temperature [15].

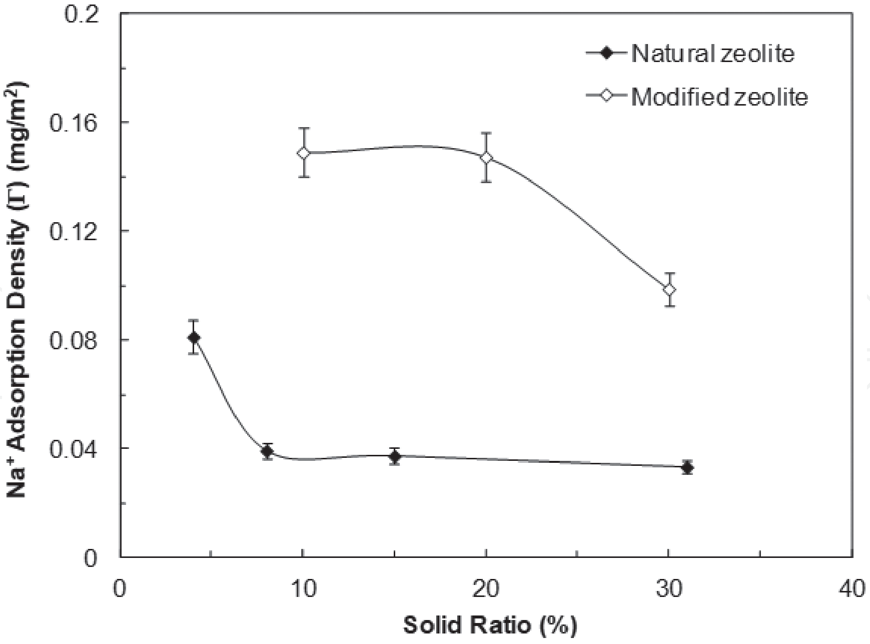


Figure 6. Na^+ adsorption density by zeolite samples versus solid ratio [15].

Ca^{2+} ions exchanged during the adsorption process. These results suggested that 0.1 M acid concentration was optimal for the modification process.

Based on the optimum acid concentration, systematic adsorption tests were carried out with zeolite sample modified at 0.1 M with different acids (**Figure 5**, right). The Na^+ removal by the modified zeolite was considerably increased. For example, the modified zeolite reduced Na^+ concentrations to approximately 180 ppm at 30% solid ratio that is acceptable for irrigation. However, zeolite modified by HAc did not change the Na^+ adsorption significantly. There was no significant difference on the SAR values for the samples due to how much Mg^{2+} and Ca^{2+} ions released from the zeolite, which could be affected by ions releasing in modification and washing process before adsorption tests.

Figure 6 shows an increase in adsorption capacity of Na^+ by the acid-modified zeolite as compared with the natural zeolite. The adsorption density (Γ) of Na^+ in the batch tests was calculated by the following formula:

$$\Gamma = \frac{(C_i - C_r) \times V}{mA} \tag{2}$$

where C_i and C_r represent the initial and residual concentrations in Na^+ (mg/L), m is the amount of zeolite used (g), V is the volume of the solution (L), A is the BET surface area (m^2/g), and Γ is the adsorption density (mg/m^2). The results in **Figure 6** evidently indicate that the modification process increased the sodium adsorption capacity of zeolite up to four times. The modified zeolite had a larger surface area than the natural zeolite. The DTA/TG, XRD, and particle size distribution results for both samples also indicated that there was no structural difference between two samples.

3. X-ray photoelectron spectroscopy (XPS) investigation of sulfuric acid modification of natural zeolite

XPS analysis of the zeolite structural composition of zeolite samples shows the presence of the O_{1s}, C_{1s}, Na_{1s}, Ca_{2p}, Si_{2p}, Al_{2p}, and K_{2p} photoelectron lines [29]. The variations of the atomic concentrations are significant as shown in **Figure 7**. With increasing sulfuric acid concentration from 0 to 5 M, the atomic proportions of each element change differently. When the acid concentration increases from 0 to 1 M and beyond, the atomic % of Na decreases from 0.6% to 0. Changes in the atomic % of Ca and Mg follow a similar trend, i.e., after treating by 1 M acid, their atomic proportion is either near zero or cannot be detected. That suggests most of the cations which are not part of the main structure and can be easily removed by acid modification. However, K cannot be totally removed after acid treatment, i.e., although the change in its atomic percentage fluctuates, the overall trend is decreasing. The proportion of Al decreases with increasing the acid concentration from 0 to 2 M and then slightly increases by 5 M acid treatment. This may due to the significant decrease in the atomic proportion of the other cations, especially at high acid concentrations. The atomic percentage of O increases from 52% (unmodified) to 60.9% after treating with 0.1 M acid and then does not change much with higher acid concentrations as Si. The atomic proportions of Al, O, and Si do not change significantly as they are the building elements of zeolite structure.

These XPS results support the sodium adsorption ratio studies. **Figure 7** shows a significant decrease in the atomic % of Ca and Mg after 0.01 M acid modification. This data agrees with the hypothesis that Ca and Mg are removed from the zeolite surface after the modification (0–1 M acid). **Figure 8** shows the trend of Si/Al ratio on the zeolite surface and [Si_{2p}-Al_{2p}] BE separation. With increasing the acid concentration, the Si/Al ratio increases from 2.99 to 4.92. However, the [Si_{2p}-Al_{2p}] BE separation increases to 29 eV when acid concentration increases from 0.01 to 0.1 M. It remains unchanged up to 2 M and finally decreases to 28.5 eV after 5 M acid modification. The increase in Si/Al atomic ratio also indicates the dealumination process occurred within the zeolite structure on the surface. Na, Mg, and Ca ions can be released into

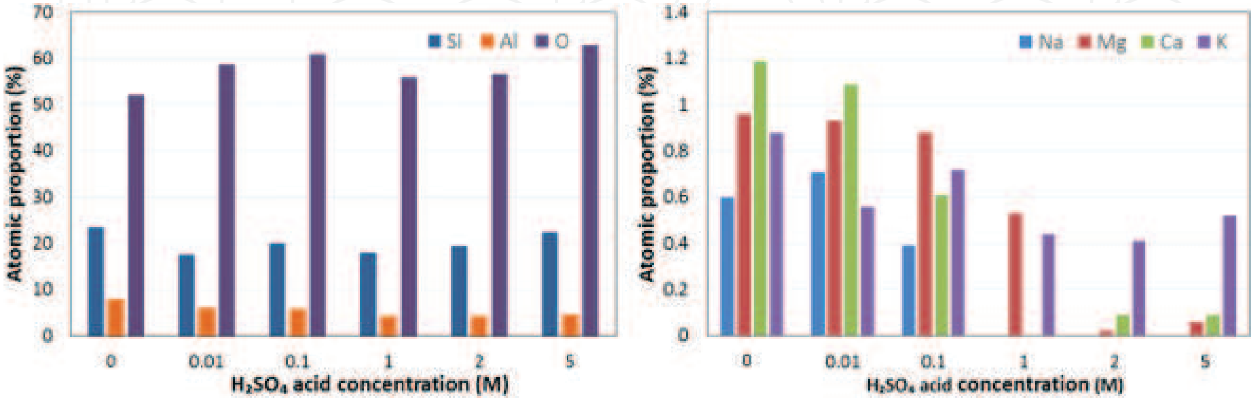


Figure 7. Effect of acid concentration on elemental atomic proportions revealed by XPS [29].

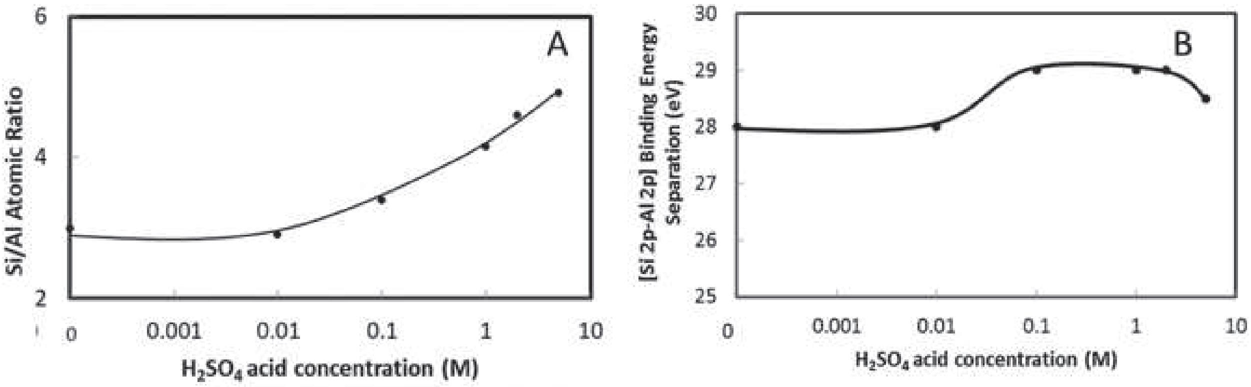


Figure 8. The effect of increasing acid concentration on Si/Al ratio (A) and [Si_{2p}-Al_{2p}] binding energy separations (B) (trend line included to illustrate the relationship) [29].

the acid solutions during the modification process. K ions as an exception (unaffected by the acid modification) remain in zeolite structure at relatively constant levels. **Figure 9** shows high-resolution scan results for Si, Al, and O which cannot be easily detected in the survey scan.

High-resolution scans for Si_{2p}, Al_{2p}, O_{1s}, K_{2p}, and Ca_{2p} of natural and sulfuric acid modification show different extents of BE increase for each element. For the building elements of zeolite, such as Si, Al, and O, the BE shifts are greater than K^+ and Ca^{2+}. The small increase in K_{2p} BE can be observed by analyzing $K_{2p3/2}$ peaks. Because of Ca removal, the progressive shifting patterns show the relative covalency-ionicity of the chemical bonds within the zeolite structure [30]. For natural zeolite studied here, the easy removal of Na from the zeolite surface after acid modification may be due to the high ionicity of the Na─O bond. Likewise, Ca─O and Mg─O ionic bonds are similarly strong, and the atomic proportion can also reduce significantly.

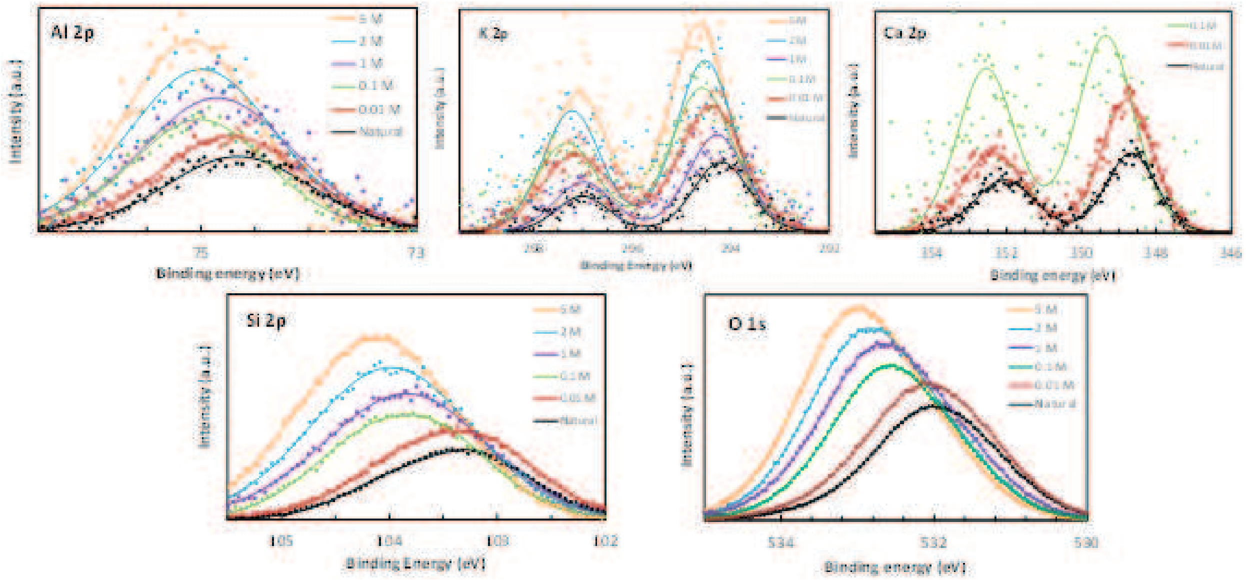


Figure 9. XPS high-resolution spectra of natural and acid-modified zeolite for Si_{2p}, Al_{2p}, O_{1s}, K_{2p}, and Ca_{2p} [29].

4. Characterization of electrokinetic properties of clinoptilolite before and after activation by sulfuric acid for treating CSG water

The change in pH of zeolite suspensions versus time can be an important parameter for the surface dissociation as well as the environmental and industrial applications. **Figure 10** shows a rapid increase in the pH value of the suspensions from pH = 5.6 of DI water (before adding natural zeolite) to 8.02 within the first 2 min. The increase in pH is due to the rapid adsorption of H^+ from solution. After the first 2 min, a very slow pH decrease to 7.13 is observed for 2 h. It shows the adsorption of H^+ in water onto the negative surface charge of zeolite. Therefore, the H^+ acts as a potential determining ion (PDI) in the electrical double layer to provide electroneutrality for the first 2 min. Besides, the H exchange with some of the cations in the lattice of zeolite structure is also the reason for the consumption of H^+ in the suspension [31]. Zeolite tends to neutralize the aqueous medium acting the H^+ desorption from the solution onto the surface of particles.

In the acidic medium, the initial pH of water was changed to 2 by 0.1 M HCl addition and then zeolite particles into the solution. The suspension pH increased to 2.4 in first 2 min and attained the equilibrium of pH 2.9 for 120 min. Al^{3+} from the octahedral sheets moves into the acid solution. They were conducive to ion exchange. Indeed, if the pH was adjusted to a lower value, dealumination process occurred throughout the measurements.

In basic medium, the initial pH of water was changed to 11.5 by 0.1 M NaOH, and then the zeolite particles were added into the solution. The suspension pH decreased to 11.27 in 2 min and equilibrated to pH = 10.5 in 120 min. The decrease in the pH value may be due to (i) the adsorption of OH^- in the suspension onto the positive charge sites, which were presented on

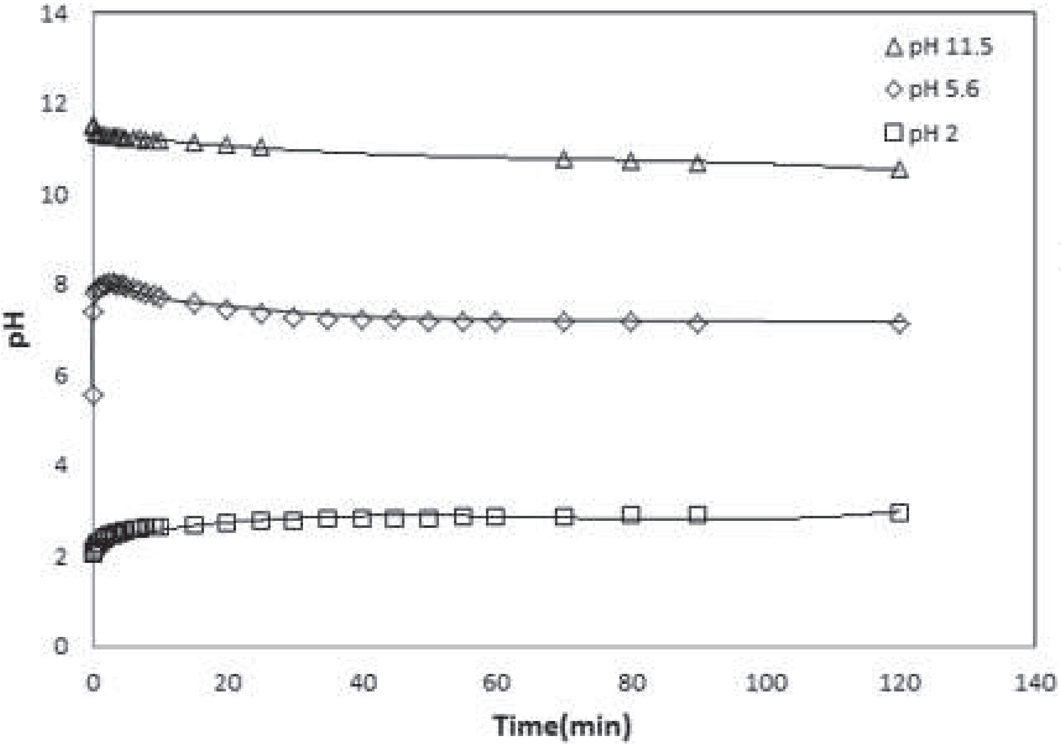


Figure 10. Transient pH profiles of suspensions of natural zeolite sample [32].

the surface of zeolite particles and exposed to water after grinding as a result of the chemical bonds breaking, and/or (ii) the desorption or transfer of the H^+ ions from —SiOH groups inside the lattice to free OH^- of H_2O into the suspension.

Since the cation exchange capacity (CEC) of zeolite mainly results from the permanently negative surface charge, surface (zeta) potential of acid-activated zeolite is an interesting parameter to be examined. As shown in **Figure 11**, the zeta potential of natural and acid-modified zeolite became more negative with the pH value increasing from 2 to 10. However, the value of zeta potential is more negative with increasing the acid concentration. In the first place, zeta potential became more negative after being modified by sulfuric acid with the concentration up to 0.1 M. With the acid concentration increased further, generally the zeta potential became less negative. The change in zeta potential versus pH was not significant at 5 M of sulfuric acid. In the neutral pH environment (pH 7), the most negative charge can be detected on the surface of zeolite modified by 0.1 M sulfuric acid.

Investigation of electrical double layer (EDL) of zeolite structure via zeta potential measurements demonstrated that H^+ plays an important role as a counterion in EDL; it adsorbs onto the inner Helmholtz plane (IHP) of the Stern layer on zeolite surface as a charge reversal. Meanwhile, OH^- was adsorbed by the outer Helmholtz plane (OHP), between the Stern layer and diffuse layer. Dealumination occurred during the acid activation process of natural zeolite [31]. It is assumed as the main reason for increasing surface charge and cation exchange capacity of zeolite surface due to the increasing of defects in zeolite crystal structure and lattice. It leads to the increase in charge vacancies. Thus, it can be assumed that the H^+ adsorption in IHP increased due to more zeolite crystal defects appeared after dealumination.

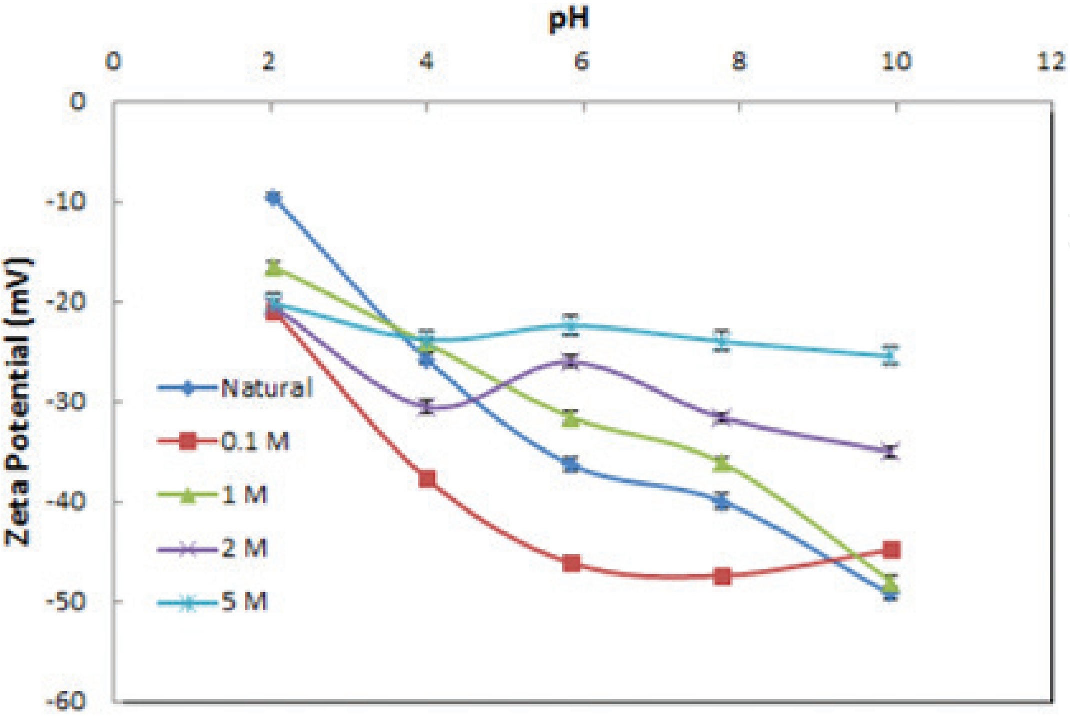


Figure 11. Surface (zeta) potential of natural and acid-modified zeolites vs. pH [32].

5. Effect of sulfuric acid modification on surface and particle properties of 4A and Na─Y synthetic zeolites

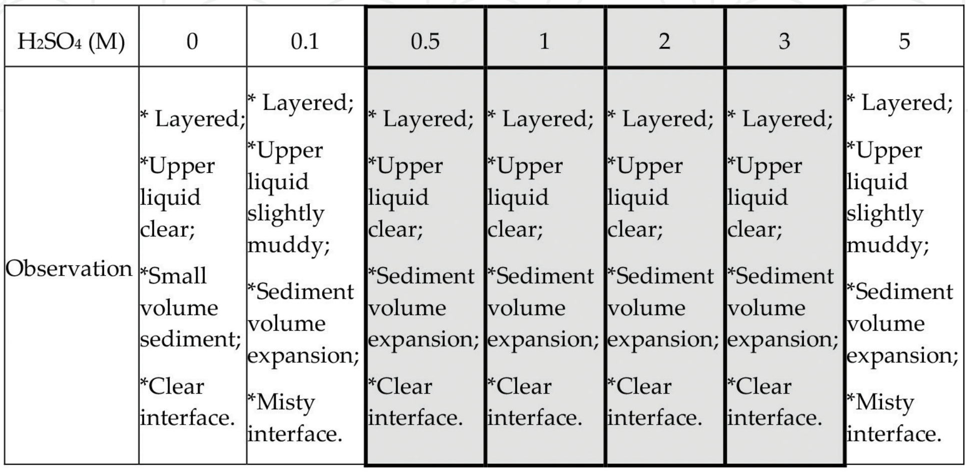
4A and Na─Y are sodium-rich synthetic zeolites, which are well-known crystalline microporous materials and widely used as solid acid catalysts and molecular sieves. Both of them have three-dimensional structures which are composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. All of the tetrahedra are interconnected with shared corners to form channels of molecular dimensions. Each AlO_4 tetrahedron bears a net charge which is neutralized by the additional positive charge from the non-framework Na^+ which is located within the channel. Because of the purity of crystalline products and the uniformity of particle sizes, synthetic zeolites are used commercially more often than natural zeolites [33]. Application of the acid modification to synthetic zeolites could provide a useful reference for understanding into improving their adsorption or ion-exchange properties, given that the effects of sulfuric acid modification of zeolite 4A and Na─Y are unknown.

5.1. Stability and resistance of 4A and Na─Y zeolites against H_2SO_4 modification

After 3-day acid modification, 4A zeolite particles were observed to become totally settled in 0 and 0.1 M H_2SO_4 solutions and partly settled in 0.2 and 0.3 M H_2SO_4 solutions. However, they completely dissolved to form a gel in the 0.5 and 1 M H_2SO_4 solutions. Low concentrations of sulfuric acid, such as 0.2 and 0.3 M, cannot dissolve the zeolite particles completely but are strong enough to break bigger 4A particles into smaller ones.

After mixing Na─Y powder with various concentrations of H_2SO_4 solutions, cloudy white suspensions were generated. Substantial settling occurred for the first day and continued to a lesser extent over the subsequent 2 days. **Table 2** describes the appearance of the suspensions after 3-day settlement.

The Na─Y powder can also be dissolved in sulfuric acid to a certain extent. The dissolution of small Na─Y particles is limited with a low concentration of sulfuric acid (0.1 M). Some of



H_2SO_4 (M)	0	0.1	0.5	1	2	3	5
Observation	* Layered; *Upper liquid clear; *Small volume sediment; *Clear interface.	* Layered; *Upper liquid slightly muddy; *Sediment volume expansion; *Misty interface.	* Layered; *Upper liquid clear; *Sediment volume expansion; *Clear interface.	* Layered; *Upper liquid clear; *Sediment volume expansion; *Clear interface.	* Layered; *Upper liquid clear; *Sediment volume expansion; *Clear interface.	* Layered; *Upper liquid clear; *Sediment volume expansion; *Clear interface.	* Layered; *Upper liquid slightly muddy; *Sediment volume expansion; *Misty interface.

Table 2. Behavior of the Na─Y suspensions after 3-day standing [34].

the Na—Y fine particles were observed to remain in a suspending state and swell significantly and then formed a diffuse solid-liquid interface. The small Na—Y particles dissolved fully at higher acid concentrations (0.5, 1, 2, and 3 M). A significant amount of acid was consumed in this process, leaving less amount of acid that was insufficient to cause the larger particles to swell to a state of suspension. That can be the reason for observing a clear solid-liquid interface. With the acid concentration increased to 5 M, not only the fine Na—Y particles were dissolved, but also a proportion of the larger particles underwent a partial dissolution, which led to swelling and suspension in solutions as being observed. Thus, the solid-liquid interface developed a diffuse appearance, like that seen at the 0.1 M acid concentrations.

As increasing the acid concentration to 0.5 M, the 4A molecular sieve could be completely dissolved and formed a gel. It was hard to observe the particle dissolution as occurred in Na—Y system. It indicates Na—Y has a strong acid resistance and is consequently more stable than 4A, possibly attributable to the higher Si/Al ratio in the structure.

5.2. Impact of H_2SO_4 concentration on solid mass in Na—Y zeolite suspensions

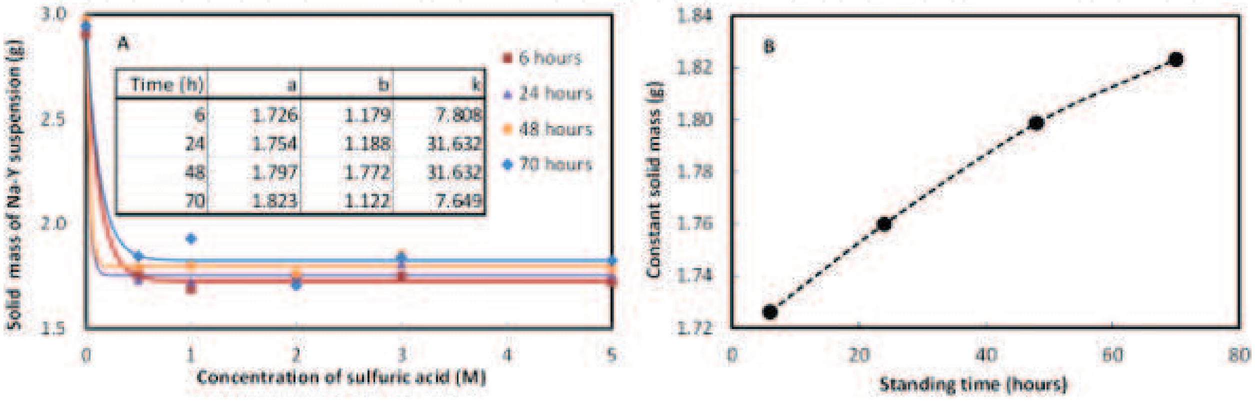
Figure 12 shows the experimental data of solid mass of the Na—Y samples left/gained over time in the suspensions after standing for 6, 24, 48, and 70 h after treatment with sulfuric acid. The data can be well fitted by the following equation of the first-order kinetics:

$$y = a + b\exp(-kx) \tag{3}$$

where y is the solid mass (obtained by filtration) of the collected Na—Y sample (grams), x is the acid concentration used in the treatment process (mole/L), and a, b, and k are the fitting parameters, with grams and L/mol as their units, respectively.

As per **Figure 12A**, the residual mass of Na—Y particles was rapidly decreased with increasing acid concentration from 0 to 0.5 M. The dissolution kinetics was fast. For concentrations higher than 0.5 M, the residual mass of Na—Y particles inclined to constant values.

Figure 12A shows that less than 6 h is required for dissolution of the acid-soluble component to reach completion. It was concluded that the acid-soluble component of Na—Y was



Time (h)	a	b	k
6	1.726	1.179	7.808
24	1.754	1.188	31.632
48	1.797	1.772	31.632
70	1.823	1.122	7.649

Figure 12. (A) Effect of H_2SO_4 concentration on mass of solid of Na—Y zeolite suspension and (B) its constant values versus standing time [34].

dissolved by sulfuric acid, after that specific component has been totally dissolved, and the residual mass did not change with increasing acid concentration. It was difficult to identify the precise nature of this dissolution by the mass loss or XRD analysis. However, it likely represented Na and Al losses based on the known structure of Na—Y. The final solid mass of the acid-treated sample increased with increasing standing time (**Figure 12B**). Therefore, it was argued that with the standing time increasing, the dissolved component partly recrystallized, leading to the mass increase. Combining with the XPS analysis shows that it is the Al content that has been reduced significantly after acid modification, as discussed in a later section. Also, the components of Na—Y which were dissolved in sulfuric acid included both Al and non-Al contents. The non-Al content was recrystallized.

XRD analysis showed the crystal structure collapsed after acid modification [34]. Comparing the untreated Na—Y to that exposed to water only, the crystal phases did not change after contacting Milli-Q water. However, the XRD results for the acid treatments showed a significant energy intensity reduction of all the crystal peaks at 0.1 M, indicating most of the crystal phases were destroyed at 0.1 M. The XRD results for 0.5–5 M acid treatments showed the same line shapes which indicated that the crystal peaks were no longer present and a transformation to noncrystalline SiO_2 took place. Therefore, the crystal structure was totally changed into a noncrystalline one after treating with sulfuric acid of >0.1 M.

5.3. XPS analysis of the effect of acid treatment on Na—Y zeolite

The results of XPS survey scans showed two different significant changes in atomic proportions of the Na—Y zeolite elements [34]: Na and Al decreased from 7.98% to 0 as the acid concentration increases from 0 to 0.5 M, but O and Si increased until the acid concentration reaches 0.5 M as well and then remained almost constant to 5 M. Sulfuric acid modifications on Na—Y zeolite could totally remove Na and Al from the surface, such that the main structural elements remaining were only Si and O. Together with the XRD results, the XPS data confirmed that Na and Al have been removed not only on the particle surface but also from the internal structure.

Figure 13 shows the detailed results of XPS high-resolution scans for the Si_{2p}, O_{1s}, and Al_{2p} regions of unmodified and modified Na—Y. The BE of Si_{2p} initially decreased by 0.10 eV after washing by Milli-Q water and then increased after 0.1 and 0.5 M sulfuric acid modification. The BE of O 1s increased with increasing acid concentration, but no BE shift in Al_{2p} was observed up to 0.1 M acid modification. No Al component was detected after being modified by 0.5 M and higher concentrations of acid. The change in O1s BE energy is explained by the interactions between the two known O bonds in the structure of Na—Y [35] (i.e., bridging oxygen

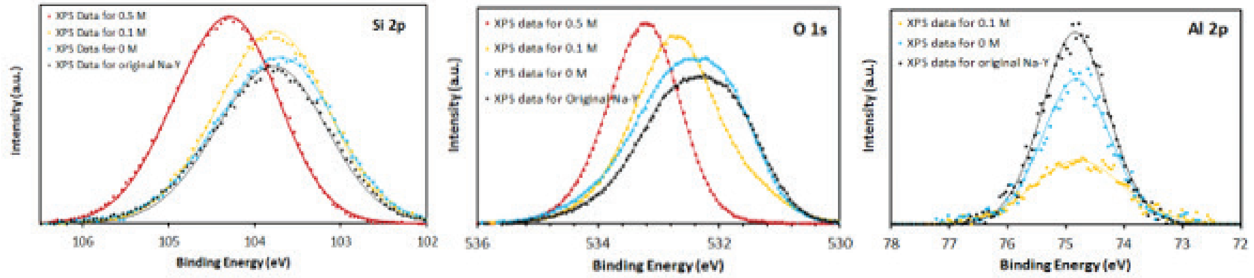


Figure 13. XPS high-resolution spectra of original and sulfuric acid-treated Na—Y for Si_{2p}, O_{1s}, and Al_{2p} [34].

incorporated in structures such as Si─O─Si and non-bridging oxygen (NBO) comprising structures such as Si─O─M (where M represents other elements such as Na, Al, etc.) and H from water [34]. There are two possible reasons for the increase in BE of Si (and O): (1) the placement of Na and Al by H and (2) partly or full destruction of the surface structure dissolved in acid solution and recrystallized into amorphous SiO_2. The presence of the recrystallized amorphous SiO_2 was detected by XRD. Similar to the case of interaction with H, the BE of both Si and O can readily increase because the electronegativity of Si is higher than Al and Na. The deconvolution of XPS high-resolution spectra of O1s [33] also demonstrates that the NBO of the Na─Y surface can be lost. It supports the argument that the surface structure of Na─Y has been dissolved and re-formed into a Si─O─Si structure after being modified by 0.5 M sulfuric acid.

Analyzing the BE shifts with the Si/Al ratio determined from survey scans, we can see after sulfuric acid modification that the BE of O and Si increases with increasing Si/Al ratio, and even at a high Si/Al ratio (Si/Al = 8.18), the BE shifts are still significant [34]. However, the BE of Al is almost unchanged in comparison with that of Si and O, no matter what acid concentration has been used or how much Al has been removed from the Na─Y structure. It may indicate that the Al─O bond is too strongly ionic in order to be affected by Na removal from the structure and H replacement.

5.4. The effect of acid treatment on the particle size of Na─Y

Figure 14 shows the effect of acid treatment on the change in Na─Y zeolite particle size. The particle size of the original Na─Y was distributed around two peaks, i.e., 4.5 μm (fine particle peak, volume in 4.21%) and 1124.7 μm (coarse particle peak, volume in 1.49%). After being washed with Milli-Q water, the fine particle peak did not change but its volume % reduced to 3.38%, while the coarse particle peak changed to 447.7 μm, and its volume decreased to 1.14%. The big particles of original Na─Y powder were formed by aggregation of smaller particles via the van der Waals force and electrostatic attractions. The large particle size fraction of the Milli-Q water-washed sample has a wider range of particle size distribution than the original Na─Y. However, it converges on the lower particle size region. The total number of particles increased because of the lager particle separation; thus, the relative volume % of the fine particles decreased. The newly created small particles did not affect the size distribution of original fine particles due to the small proportion of larger particles.

After 0.1 M acid modification, no particles larger than 1000 μm remained in solutions, and the volume % of coarse particles increased to 1.61%. The particles might be further separated, and the Na─Y structure partly dissolved in 0.1 M acid due to the dealumination process. Another type of stable silicon aluminum oxide with a particle size distributed at 399.1 μm was formed by the partly de-aluminized Na─Y.

There was no significant change of fine particle distribution after 0.5 M sulfuric acid modification. However, the peak position of coarse particle distribution has shifted to a smaller particle size region. Combined analysis of XRD and XPS revealed neither the Na─Y crystal phases nor Al was present in this sample [34]. It agrees with the experimental results showing that the structure of Na─Y was totally de-aluminized with increasing concentration of sulfuric acid to a certain level. However, the remaining Si-O structures still remained, with a size distribution peaked at 251.8 μm.

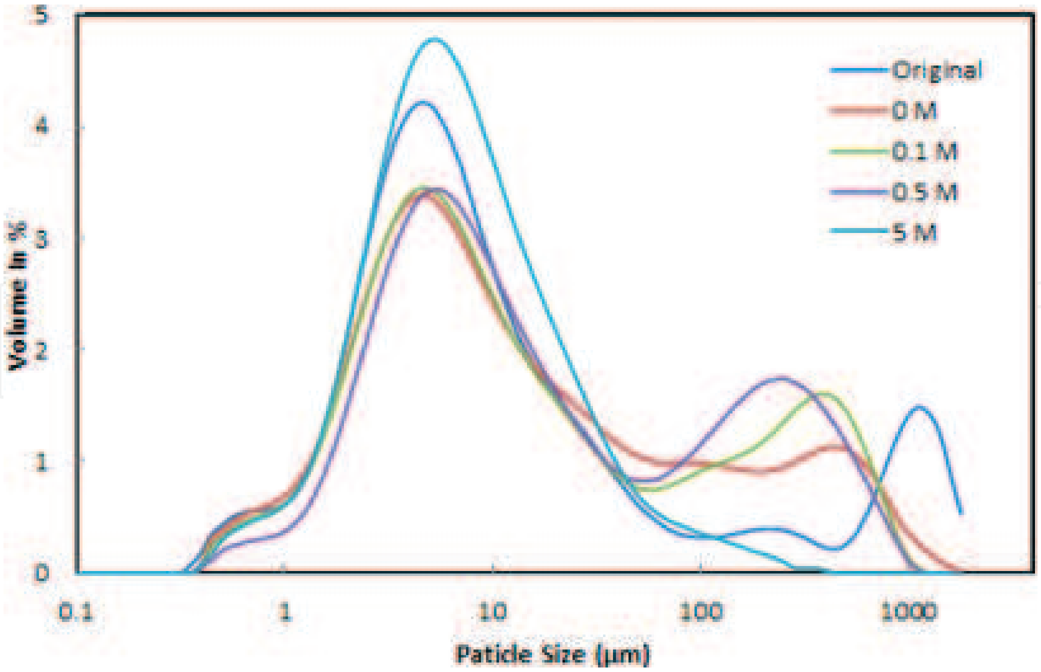


Figure 14. Particle size distribution of original and acid-treated Na—Y [34].

Comparing with 0.5 M acid modification, the volume % of fine particles increased greatly after treating with 5 M acid. The distribution of the coarse particles disappeared, but the fine particle size distribution remained the same. Thus, coarse particles dissolved to fine particles by 5 M acid modification, and the newly generated fine particles displayed a similar size distribution as the original fine particles. As per both XRD and XPS analyses for the 5 M acid-modified sample, there were no crystal phases, and Al was present in the sample, and the Si atomic ratio was slightly lower than for the case of the 0.5 M modification. Therefore, after the 5 M acid modification, not only was the Na—Y structure but also the remaining Si—O structure was fully destroyed by dealumination. It is the reason for the disappearance of the coarse particles. The dissolved Si and O recrystallized and formed an amorphous SiO_2 with a particle size distribution peaked at 5.0 μm.

As there was a constant peak of fine particle size at 4.5–5.0 μm in each sample, this particle size did not characterize the particles of the crystal phase of original Na—Y. On the contrary, the coarse particles with changing size from 1124.7 to 399.1 μm when the acid concentration increased from 0 to 0.1 M could be considered as the characteristic peak of the silica-alumina structure in Na—Y crystal phase. Even if there was a coarse particle peak at 251.8 μm detected for the 0.5 M acid-modified sample, these particles would not be considered as representative of the Na—Y crystal phase.

6. Conclusions

The major objective of this chapter is to investigate the potential use of natural and acid-activated zeolites (clinoptilolite) for CSG water treatment. Both natural and synthetic zeolites have been studied in unchanged and acid-activated forms in regard to surface composition, surface binding energy, and surface charge properties. The CSG water treatment study by applying the natural and acid-activated zeolites has been completed. The possibility of reducing the sodium concentration and SAR of CSG water using natural zeolite has been demonstrated.

Natural zeolite containing mainly clinoptilolite can be modified and activated by different concentrations of sulfuric acid. The XPS analysis of the natural zeolite and acid-modified zeolite shows significant changes in the surface properties of natural zeolite because of acid modification. Increasing acid concentration from 0 to 5 M can increase the Si/Al ratio on the zeolite surface from 2.99 up to 4.92. Cations within the zeolite atomic structure exchange with hydrogen ion, weakening the zeolite surface structure. The structural bonds become relatively covalent after acid modification and can be indicated by the BE increase of each main element. High-resolution spectral analysis also shows that the covalent nature of the remaining bonds within the structure can be increased by the ionic bond breakage inside the modified zeolite. The surface properties of clinoptilolite-type natural zeolite can be affected by sulfuric treatment which causes zeolite surface charge more pH-independent by increasing the acid concentration. Based on the results obtained from these studies, dealumination can be the main reason for the increase in surface charge of the zeolite. The hydrogen ions adsorb onto the negatively charged surface sites, reducing the surface potential and charge density. The adsorbed hydrogen ions can be very useful for neutralizing bicarbonate ions in CSG water, thereby reducing its pH.

Examining the dissolution and recrystallization of the zeolite particles, particle size measurement, XRD, and XPS have successfully been applied for investigating the changes in structure and properties of Na-rich synthetic 4A and Na─Y zeolites by modifying with H_2SO_4 at room temperature. The XRD analysis shows the acid modification can cause structural damage, where sodium cations can be removed and dealumination occurs as dissolution progress takes place, thereby the main tetrahedral structure is affected. The Si/Al atomic ratio increases from 2.94 at 0 M to 8.18 at 0.1 M, and a significant binding energy (BE) shift of Si and O can be observed even at a high Si/Al ratio. A relatively low acid concentration (lower than 0.3 M) can be used in the modification of 4A zeolite (low Si/Al ratio) because higher acid concentrations dissolve and can destroy it completely. Na─Y zeolite (high Si/Al ratio) has stronger acid resistivity than 4A zeolite and can be treated with H_2SO_4 up to 5 M. For both 4A and Na─Y zeolites, the acid modification produces dissolution (of both Si and Al) of the first-order fast kinetics and then recrystallization comes about. Gel generation after the acid dissolution can be homogenous or heterogeneous. The constant mass of solid, which left in solution after a long time formed by the recrystallization, increases with time. However, neither Al nor Na participates in the recrystallization process, only the dissolved Si gradually recrystallizes with the standing time goes on once the solubility of Na─Y achieves a threshold value. The Al and Na sites of Na─Y zeolite structure can be completely removed when the acid concentration reaches 0.5 M, which is observed as the threshold value for the Na─Y zeolite. The peak particle size of the size distribution which can characterize the change of the Na─Y crystal phase before and after acid modification is found to vary from 1124.7 to 399.4 μm.

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Conflict of interest

There is no conflict of interest.

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