Toward zero waste to landfill: an effective method for recycling zeolite waste from refinery industry

K Homchuen\textsuperscript{1}, R Anuwattana\textsuperscript{2}, N Limphitakphong\textsuperscript{3} and O Chavalparit \textsuperscript{1,3}

\textsuperscript{1}Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330 Thailand
\textsuperscript{2}Environment and Resources Department, Thailand Institute of Scientific and Technological Research, Pathumthani, 12120 Thailand
\textsuperscript{3}Research Unit of Environmental Management and Sustainable Industry, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330 Thailand

Email: orathai.c@chula.ac.th

Abstract. One-third of landfill waste of refinery plant in Thailand was spent chloride zeolite, which wastes a huge of land, cost and time for handling. Toward zero waste to landfill, this study was aimed at determining an effective method for recycling zeolite waste by comparing the chemical process with the electrochemical process. To investigate the optimum conditions of both processes, concentration of chemical solution and reaction time were carried out for the former, while the latter varied in term of current density, initial pH of water, and reaction time. The results stated that regenerating zeolite waste from refinery industry in Thailand should be done through the chemical process with alkaline solution because it provided the best chloride adsorption efficiency with cost the least. A successful recycling will be beneficial not only in reducing the amount of landfill waste but also in reducing material and disposal costs and consumption of natural resources as well.

1. Introduction
Most of refinery wastes are difficult to manage as it contaminates with metal and oil [1]. It is classified as hazardous waste which is usually used just once and disposed to secure landfill directly even some of them might be reusable or recyclable. Among several types of landfill waste from refinery industry, one-third of them is spent chloride zeolite generated in gas separation unit for removing hydrogen chloride (HCl) gas from hydrogen stream since it can combine with ammonia to form an ammonium chloride salt resulting in corrosion and fouling or pressure drop in the process consequently [2].

To improve the current waste management system toward zero waste to landfill, sustainable waste management such as 3Rs (reduce, reuse, recycle) strategy should be implemented. Some researchers have used sodium chloride (NaCl) or sodium hydroxide (NaOH) solutions to regenerate zeolites and state that zeolites can nearly be completely regenerated at pH 11-12, while some have been introduced for regenerating spent zeolite via electrochemical method because of its less adsorbent loss, in-situ regeneration and, high regeneration efficiency [3,4,5,6,7].

This study, therefore, aimed to determine the suitable method for recycling zeolite waste from refinery industry in Thailand. Two regeneration methods (chemical and electrochemical process) were examined and compared to find the most effective way. Properties of fresh, spent, and regenerated...
zeolites were tested. On each experiment, optimal conditions were measured, and an efficiency of chloride adsorption, a residual chloride in regenerated zeolite, and an operation cost were investigated.

2. Materials and method

2.1. Materials
- Fresh and spent chloride zeolites obtained from refinery plant in Rayong Province.
- An electrochemical reactor with dimension of 5 cm x 1 cm x 10 cm was set up by placing flat and rectangular Ti/Pt electrodes with surface area of 25 cm2 in parallel at a separation distance of 1 cm and putting 10 grams of zeolite waste in the middle.
- Chemicals; Sulfuric acid (H₂SO₄), Nitric acid (HNO₃) and Sodium hydroxide (NaOH), were used for adjustment the pH of water and in the regeneration of chemical process.

2.2. Experimental design and analytical method
The experiment of chemical process was designed by varying a concentration of chemical and reaction time, whilst electrochemical process was stimulated for understanding a range of current density, initial pH and reaction time. Both experiments were operated at room temperature of 28 °C.

The characteristics of all zeolites were analysed by X-ray fluorescence spectroscopy (XRF). The surface area, pore size and pore volume were measured via Brunauer-Emmett-Teller method (BET). The morphology was analysed by scanning electron microscopy (SEM). The crystalline structure was tested by X-ray diffraction Spectroscopy (XRD) and the concentration of chloride was determined according to EPA method.

3. Results and discussion

3.1. Properties of zeolite before and after regenerating
To ensure a probability of recycling zeolite, physicochemical characteristics and crystalline structure of the zeolite waste were examined before regenerating to compare with the fresh one. It was found that chemical compositions of both substances were similar, except the composition of chloride as zeolite waste would contain a higher percentage of chloride after spending in HCl removal process as shown in table 1. In addition, the structure of each zeolite in figure 1 was in a crystal form with size of 2 - 4.5 µm. The photograph of zeolite regenerated in alkaline solution (figure 1F, 1G, 1I) was very similar with the fresh one. Thus, it might be possible for recycling zeolite waste instead of landfilling the fresh one once used for removing HCl.

3.2. Optimum conditions of zeolite regeneration via chemical process
In total, 69 experiments were run to examine the effect of each parameter on the substances. Of that, 25 operations were set up by varying a concentration of chemicals from 0.1 to 3 molar (M), and the reminder was for testing a reaction time from 10 to 150 minutes (min). As demonstrated in figure 2, regenerating with acid solution (H₂SO₄ and HNO₃) provided a higher chloride desorption efficiency than that using alkaline solution (NaOH).

An increasing of chemical’s concentration affected a decreasing of chloride residue in regenerated zeolite, which meant chloride desorption efficiency increased. However, pH of the solutions will increase as well because sodium-chloride in spent zeolite was released [8]. The best option for regenerating zeolite was found at 0.3M for all three solutions, then such concentration was used to study the effect of reaction time consequently. The optimal reaction time of regeneration with 3M of H₂SO₄ was 50 min with chloride residual in regenerated zeolite of 1.91 mg chloride/g zeolite, while regenerating with HNO₃ and NaOH required 60 min and remained more chloride residual in regenerated zeolite. However, the crystalline structure after regenerating emphasized that spent zeolite regenerated in alkaline condition looked very likely to conform to the fresh zeolite, especially the crystalline structure of zeolite regenerated with NaOH (figure 2-lower).
Table 1. Physicochemical characteristics of zeolites before and after regenerating.

| Substance            | Chemical composition (wt.%) | Surface area (m²/g) | Pore volume (cc/g) | Pore size Å |
|----------------------|-----------------------------|---------------------|--------------------|-------------|
|                      | Cl  | SiO₂ | Al₂O₃ | Na₂O | MgO | SO₃ |                      |                      |                  |
| **Before Regenerating** |     |      |       |      |     |     |                      |                      |                  |
| Fresh zeolite        | 0.16 | 46.1 | 25.7  | 15.2 | 2.3 | 0.85| 517                  | 0.421              | 32.54          |
| Zeolite waste        | 2.13 | 43.8 | 27.3  | 13.6 | 2.0 | 0.84| 436                  | 0.379              | 34.80          |
| **After Regenerating via chemical method** |     |      |       |      |     |     |                      |                      |                  |
| H₂SO₄ 0.3 M          | 0.18 | 40.7 | 15.7  | 6.63 | 2.0 | 1.79| 354                  | 0.304              | 31.52          |
| HNO₃ 0.3 M           | 0.25 | 41.5 | 20.4  | 9.54 | 2.7 | -   | 383                  | 0.425              | 35.82          |
| NaOH 0.3 M           | 0.40 | 42.9 | 25.3  | 14.1 | 2.1 | -   | 435                  | 0.418              | 34.87          |
| **After Regenerating via electrochemical method** |     |      |       |      |     |     |                      |                      |                  |
| pH 1                 | 0.21 | 39.7 | 20.3  | 8.21 | 1.83| 1.81| 390                  | 0.322              | 34.11          |
| pH 5                 | 0.39 | 40.3 | 22.1  | 9.25 | 1.89| 1.67| 394                  | 0.323              | 36.52          |
| pH 8.1               | 0.54 | 41.9 | 25.1  | 11.8 | 1.96| 0.11| 415                  | 0.396              | 35.01          |
| pH 10                | 0.47 | 41.5 | 24.9  | 12.5 | 1.94| -   | 430                  | 0.415              | 34.82          |
| pH 13.6              | 0.43 | 40.6 | 24.1  | 13.2 | 2.00| -   | 431                  | 0.418              | 34.83          |

Figure 1. Crystalline structure of zeolites before and after regenerating. (A) Fresh zeolite (B) Spent zeolite (C-G) Regenerated zeolite via electrochemical process at pH 1,5,8,10,13.6 (H-J) Regenerated zeolite via chemical process with H₂SO₄, HNO₃ and NaOH
In conclusion, the optimum condition of chemical process was regenerating zeolite waste with NaOH at concentration of 0.3 M for 60 min. With such condition, the amount of residual chloride in regenerated zeolite was 3.86 mg chloride/g zeolite with chloride adsorption efficiency of 82%.

3.3. Optimum conditions of zeolite regeneration via electrochemical process

In total, 32 electrochemical batches were run to examine the effect of each parameter on the substances. Of that, 13 operations were set up by varying a current density from 4 to 100 mA/cm$^2$, 10 batches were built for testing an initial pH in a range of 1 – 13.6, and the reminder was for testing a reaction time varied from 0 to 40 min. As demonstrated in figure 3, spent zeolite regenerated in alkaline condition looked very likely to conform to the fresh zeolite, especially the crystalline structure of zeolite regenerated at initial pH of 10 (figure 3A) and the lowest point of electrical resistance (50 ohm) was given at the current density of 20 mA/cm$^2$ and it was a turning point for either chloride residual in regenerated zeolite or chloride desorption efficiency as well (figure 3B, 3C). Using acid solution took less reaction time than operating on neutral or alkaline solution (figure 3D) and the results agree with Liu et al (2008) and Elsener and Angst (2007) that indicated an increasing of chloride removal efficiency or a decreasing of chloride residue in regenerated zeolite with the reaction time increased.

To sum up, the optimum condition of electrochemical process was regenerating zeolite waste with Ti/Pt electrodes at initial pH of 10 and current density of 20 mA/cm$^2$ for 25 min. With such condition, the amount of residual chloride in regenerated zeolite was 4.89 mg chloride/g zeolite with chloride adsorption efficiency of 77%.

3.4. Cost of operation

Referring to an interview with project manager of zero waste to landfill for refinery plant, one-third of total waste to secure landfill was zeolite. A million of note was paid for handling such waste properly annually due to a high cost of secure landfill of 3,200 THB/kg of waste. In this study, cost of regenerating via chemical process was accounted only in term of chemical used, while electrochemical process involved cost of chemical and power. It was found that for every kilogram of zeolite regenerated, only 10 THB was paid for regenerating zeolite waste with NaOH solution at the optimum conditions. Whilst to reach the optimum conditions of electrochemical process, around 160 THB/kg of zeolite regenerated was required mainly for electricity bill.
Figure 2. Optimum conditions of regenerating zeolite waste via chemical process. (Upper) Effect of chemical concentration on chemical regeneration (Middle) Effect of reaction time on chemical regeneration (Lower) Crystalline structure after regeneration

Figure 3. Optimum conditions of regenerating zeolite waste via electrochemical process. (A) Crystalline structure after regeneration (B) Effect of current density on electrical resistance (C) Effect of current density on electrochemical regeneration (D) Effect of reaction time on electrochemical regeneration

4. Summary
To improve waste management system toward zero waste to landfill, sustainable waste management such as 3Rs strategy was needed to determine a suitable method for recycling zeolite waste from refinery industry in Thailand. Chemical and electrochemical processes were introduced for regenerating the spent zeolite instead of using a fresh zeolite once as usual. The optimum conditions of both processes were examined and the chloride adsorption efficiency and cost of operation at the optimum conditions were compared to identify the most effective method of regeneration. From all point of view; chloride adsorption efficiency, residual chloride in regenerated zeolite and operation cost, regenerating zeolite waste via chemical process at the optimum conditions was more effective than that of electrochemical process. Therefore, chemical process is an alternative effective option for regenerating zeolite waste from refinery industry. Moreover, the regeneration process has shown several advantages such as a reduction of waste, time and cost for landfilling, a reduction of natural resources for producing a fresh zeolite, and a saving cost of purchasing a fresh zeolite. The further
study might be focused on an application of zeolite regenerated with sulfuric acid solution because the higher sulfur residual in regenerated zeolite might be beneficial for toxic or hydrogen sulfide adsorption.

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