The comparison of the alkali-treated and acid-treated naturally mined Philippine zeolite for adsorption of heavy metals in highly polluted waters

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Abstract. Natural zeolite can be modified by single or combined treatment of heating and chemical modification using acids, bases, and inorganic salts. In this study, the Philippine natural zeolite (PNZ) was modified with alkali and acidic solution. The alkali-treatment and acid treatment used sodium hydroxide (NaOH) and acetic acid (CH₃COOH) as chemical modifier respectively. Various concentration of the solution (1M and 2M) and temperature (25°C and 50°C) was used during modification of the PNZ. The XRD of Na-PNZ and Ac-PNZ shows mineralogy of clinoptilolite and mordenite phases of the natural zeolite. The SEM images shows porous and plate-like morphologies of both modified materials. These property shows surfaces for adsorption of metals from wastewater solutions. The Na-PNZ and Ac-PNZ was used as adsorbents for the treatment of synthesized copper solution. The copper uptake of Na-PNZ from an aqueous solution is higher compared to the Ac-PNZ at 99.58%. The adsorption capacity sequence of the modified materials are as follows, 1M Na-PNZ > 2M Na-PNZ > 1M Ac-PNZ > 2M Ac-PNZ. The temperature used in the modification appears to have a significant effect on the adsorption capacity of the modified PNZ samples, the increase in temperatures resulted to a decrease in the uptake of copper.

1. Introduction

Natural zeolite can be modified by single or combined treatment of heating and chemical modification using acids, bases, and inorganic salts. Chemical and thermal treatment of zeolite may result in cation migration and thus affect the cation location and pore opening. Sorbent properties are manipulated during zeolite modification by the application of “pore engineering”, which is a popular term for the methods used in modifying zeolites [1]. The adsorption characteristics of any zeolite are dependent upon the detailed chemical and structural properties of the adsorbent. The composition, the Si/Al ratio, cation type, number and location also influence the adsorption. These properties can be further modified by chemical treatments to improve the separation efficiency of the unmodified, raw natural zeolite. Treatments by acids and bases, and surfactant impregnation by ion exchange are among the commonly employed methods to modify and change the hydrophilic/hydrophobic properties of the zeolites [1].

Alkali treatment of zeolites causes desilication, resulting to the lowering of the Si/Al ratio (SAR) and an increase in the relative concentration of cations in the framework. Due to a higher negative charge within the framework, the metal adsorption capacity of the zeolite thus improves. A research by Ouki et al. [4], was conducted to investigate the effect of alkali treatment to the exchange capacity...
of clinoptilolite and chabazite, two known natural zeolites. The modified zeolites were used to treat samples containing Pb$^{2+}$ and Cd$^{2+}$ ions. Results show an increase in the exchange capacity of both zeolites as compared to their natural counterpart [3].

Different treatments however result to different effects on the exchange capacity of the zeolites. Based on the same study by Ouki [4] the zeolites which undergone alkaline treatment has an inferior or nearly equivalent exchange capacity as compared to zeolites treated with salt solution at ambient temperature. A research by Panayotava, studying the uptake of Cu$^{2+}$ of the alkaline and salt treated clinoptilolite at ambient temperatures reported the same result. The Cu$^{2+}$exchange capacity of the alkaline and salt treated zeolite was said to be equivalent. [3-4] The modification using the combination of salt and alkali solution resulted also to mixed results depending on the type of zeolite, the metal ion type, and the metal ion concentration. [3].

Acid treatment on natural zeolites results to the removal of impurities blocking the pores of the zeolites, thus resulting to further elimination of cations to change into H-form and finally dealuminate the structure. Acid wash is said to have great influence on the effective pore volume of the zeolite as well to its surface area. However, zeolite treatment using acid has a detrimental effect on the minerals’ metal adsorption capacity. Acid treatment causes an increase in the Si/Al ratio in zeolite thus decreasing its net negative charge. Also, in the event of a natural zeolite having K$^+$ ions, acid treatment increases the relative concentration of K$^+$thus reducing the easily exchangeable Na$^+$ ions because of the decrease of the Na$^+/K^+$ ratio. The research conducted by Panayotova [5] reported a lower exchange capacity of acid treated clinoptilolite as compared to untreated clinoptilolite. [1-2].

To summarize, researches show a similar trend on the effect of the different modification on the exchange capacity and porosity of the zeolites. The combination of salt and alkaline treatments, at ambient temperature, shows the collaboration in increasing the metal adsorption capacity of the zeolite. Natural zeolites pre-treated with salt and subsequently treated with alkali solution reported a superior exchange capacity as compared to zeolites treated only with salt or only with alkali solution. However, treatment using strong acid decreases the metal adsorption capacity of the zeolite. Acid treated zeolites has an inferior exchange capacity to that of untreated or natural zeolites. [1][2][3]

This study will explore the applicability of naturally mined Philippine zeolite (PNZ) modified by alkali (NaOH) and acid treatment (CH$_3$COOH) to the treatment of contaminated wastewater with from industrial effluents.

2. Experimental

The material was acquired from a zeolite mine, SAILE Industries, Inc., located in Mangatarem, Pangasinan, Philippines. The zeolite sample was dried and grinded to achieve 80% passing of 0.5mm particle size using a 0.5 mm laboratory grade test sieve. It was then washed and dried at 110$^\circ$C for 12h. The chemicals used were technical grade, supplied by Alyson’s Chemical Enterprises, Inc. such as NaOH pellets, CuSO$_4$, and CH$_3$COOH. All solutions were prepared using a deionized water.

2.1 Modification of the PNZ

The PNZ was modified into two treatments – acid and alkaline modification using acetic acid (1M and 2M CH$_3$COOH) and sodium hydroxide (1M and 2M NaOH) respectively. Thirty (30) grams of PNZ was mixed in a 200 mL of the modifying solution at 200 rpm at RT for 4h. The resulting modified materials are named as Na-PNZ and Ac-PNZ for alkali treated and acid treated materials respectively.

2.2 Characterization of modified PNZ

The surface morphology of the modified materials was analysed using Hitachi S3400N scanning electron microscope. The mineralogy of the samples was determined using X-ray diffractometer (Shimadzu Maxima XRD-7000).
2.3 Batch Adsorption Studies
The modified PNZ materials were assessed to determine its adsorption efficiency for copper. Five (5) grams of the Na-PNZ and Ac-PNZ samples were mixed separately with synthesized 50mL of synthesized copper solution (50 ppm). The solutions were mixed at 200 rpm for one hour at ambient temperature using a Corning hot plate. All the eluate was tested for copper concentration using Shimadzu AA6300 Atomic Absorption Spectrometer.

3. Results and discussion

3.1 Morphology of the modified PNZ
The SEM images of Na-PNZ and Ac-PNZ using a scanning electron microscope are shown in Figure 1. The Na-PNZ exhibits a platy morphology. The Ac-PNZ on the other hand exhibits a very smooth globular morphology. From these morphologies, the adsorption of each sample can be deduced. Since Na-PNZ exhibits a rough surface, the adsorption sites are expected to be higher, as compared to the Ac-PNZ with a smoother surface. This translates to the results that the Na-PNZ have high uptake as compared to the Ac-PNZ shown in Figure 3.

![Figure 1. SEM images of (a) Na-PNZ and (b) Ac-PNZ at 10,000x magnification.](image)

3.2 X-Ray diffraction patterns
Shown in Fig. 2, the major crystalline mineral phases of the Na-PNZ and Ac-PNZ are clinoptilolite (Na,K,Ca)2·3Al3(Al,Si)2Si13O36·12H2O and mordenite (Ca2 Na6 K2)Al2Si10O24·H2O. There are four distinct peaks observed in the X-ray diffraction patterns of Na-PNZ and Ac-PNZ. These peaks are similarly observed at 10, 22.2 and 27.8 and 35 2θ values. Guide lines superimposed on these peaks are shown in the Figure 5. There are shifts of some peaks attributed to the PNZ modification processes which resulted from the changes in the SAR of the modified materials. Acidic and alkaline modifications altered the SAR of the PNZ detected in the XRD analyses. Acid treatment causes an increase in the SAR and decreases its net negative charge [1-2], while alkaline treatment decreases the SAR of the PNZ.

3.3 The effect of acid and base treatment on the adsorption capacity and metal uptake
Fig. 3 shows the effect of the modification of PNZ with acidic and alkaline treatments of varying concentrations of acetic acid (CHOOH) and sodium hydroxide (NaOH), and modification temperatures. Results show high copper recovery using the NaOH modified zeolite, while a significantly lower copper uptake was observed for PNZ modified using acetic acid. The Na-PNZ recorded an uptake of more than 99% copper uptake. Under alkaline conditions, the treatment causes desilication for the zeolite sample, which in turn results to the lowering of the silicon-to-aluminum ratio, SAR, and an increase in the relative concentration of cations in the framework. Due to a higher negative charge within the framework, the metal adsorption capacity of the zeolite
thus improves. According to Ouki [4], different treatment however results to different exchange capacity of the zeolite. Moreover, if the contact time is not enough, the desired performance in recovery is not achieved and not exhibited.

![XRD patterns](image)

**Figure 2.** XRD patterns of (a) Na-PNZ and (b) Ac-PNZ at 10,000x magnification.

Acid treatment on natural zeolites improves the pore volume as well to its surface area of the material [2]. Soaking with acid results to the removal of impurities blocking the pores of the zeolites, thus resulting to further elimination of cations to change into H-form and finally dealuminate the structure. Acid treatment causes an increase in the silicon-to-aluminum ratio, SAR, thus decreasing its net negative charge. In the event of a natural zeolite having K+ ions, acid treatment increases the relative concentration of K+, reducing the easily exchangeable Na+ ions because of the decrease of the Na+/K+ ratio. As shown in Fig. 3, as the concentration of the modifying solution of acetic acid increases, the copper uptake decreases. The acid treatment exhibited detrimental effect on the adsorption capacity of the Ac-PNZ.
Figure 3. Copper uptake of different types of modified PNZ samples (Na-PNZ and Ac-PNZ) at varying concentrations and temperatures.

Figure 4. Effect of solution concentration used in modification to the %recovery of Cu of modified zeolite. Red – Ac-PNZ (CH3COOH), Blue – Na-PNZ (NaOH).

It is also important to note that increasing the concentration of the solution, either acidic or basic, results to a decrease in the metal recovery of the zeolite samples. Shown in Figure 4, the Na-PNZ (1M NaOH) held at ambient temperature has an uptake of 99.57% which decreased to 98.89% as the concentration of NaOH is doubled. Similar with the Ac-PNZ samples, the recovery of Ac-PNZ (1M CHCOOH) at ambient temperature is 74.90% but decreased to 71.94% at an increase of acid concentration to 2M at the same temperature. This is attributed to the structural changes occurring during the modification process, changing the SAR, and consequently the net charge of the material resulting to an improved or decreased heavy metal recovery from the test solution [1-2].
Figure 5. Effect of temperature on the recovery of copper of modified zeolites. Red – Ac-PNZ (CH$_3$COOH), Blue – Na-PNZ (NaOH)

In Figure 5, the temperature used in the modification technique appears to have a significant effect on the adsorption capacity of the modified PNZ samples but is not pronounced enough to be observed. For 1M NaOH, 2M NaOH and 2M CHCOOH - modified PNZ, the increase in temperature at constant acid/base concentrations resulted to a decrease in the uptake of copper from the solution.

The order of the performance of modified PNZ samples according to the copper uptake (50 ppm copper concentration) are arranged as follows, Na-PNZ (1M) >>> Ac-PNZ (1M). This order agrees to the current literature available that acid treated zeolite exhibits inferior adsorption capacity to that of alkali-treated natural zeolites [1].

4. Conclusion
The PNZ was successfully modified using acid-treatment with CH$_3$COOH (Ac-PNZ) and alkali-treatment with NaOH (Na-PNZ). It was observed that modification by acid-treatment decreases the metal uptake of the adsorbent, PNZ, due to the change in the crystal framework (shift of XRD peaks) of the PNZ brought about by the acid modification. The surface morphology of Na-PNZ and Ac-PNZ indicates a rough and smooth surface respectively. The Na-PNZ modified with 1M NaOH, 25°C has a higher metal uptake compared with the Ac-PNZ.

Acknowledgment
The researchers would like to acknowledge SAILE Industries Inc., for providing us the necessary zeolite samples for the project. The faculty and staff of the Department of Mining, Metallurgical and Materials of the University of the Philippines in Diliman, Quezon City for the facility use in the material modification, characterization and adsorption studies of the modified PNZ adsorbent materials.

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