The effect on the zeta potential of surface modified Philippine natural zeolites (SM-PNZ) for the adsorption of anionic solutions

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Abstract. This study investigates the effect of surface modification on the surface charge of the natural zeolites (PNZ) from SAILE Industries in the Philippines by utilizing the zeta-potential technique. The SM-PNZ is prepared to be utilized in the adsorption of anionic aqueous solutions like gold cyanide [Au(CN)₂⁻] solutions from gold extractive companies. The experiment was designed by converting natural zeolites into its Na-form and modified using cetyl trimethylammonium bromide (CTAB), a micelles-forming surfactant, with dosages equal to 100% and 200% of ECEC (external cationic exchange capacity) of the PNZ. Further characterization of the adsorbents by SEM shows a plate-like morphology. The zeta-potential of the SM-PNZ material shows a decreased negative surface compared with the unmodified PNZ. The percentage recovery of gold cyanide to the PNZ, SM-PNZ (100) and SM-PNZ (200) was 22%, 45% and 40% respectively. Surface modification has shown to improve the adsorption of the PNZ by decreasing the negative potential of the PNZ and increasing the affinity of the SM-PNZ to anionic solutions.

1. Introduction

Naturally, zeolites have negative charges even in acidic conditions due to its substitutions of cations within the lattice, lattice imperfections, and broken Si-O-Si bonds generated from grinding. Also, zeolite is found to be permanently charged due to isomorphous substitution [1-3]. Negative charges are decreased when natural zeolite is modified in alkali pH, due to exchange of Na⁺ cations, which relatively has the weakest bond and nearest locality to the surface. Al and Si were observed to dissolve only in acidic solutions with strong electrolytic property at low zeolite amounts due to the strong interaction between zeolite protons and surface hydroxyl groups. Lastly, it was found out that zeolite, whether natural or modified, can be used as buffer for strong acid-weak base solution. Thus, varying the pH affects the ion exchange behavior of zeolite, aside from other factors such as temperature, cation type, and heat of solution [1].

A different study by Celik [2] determined the electrokinetic properties of natural zeolite, specifically clinoptilolite. Isoelectric properties are important factors to consider since it governs adsorption and other related processes [2]. Since surface potential cannot be measured directly, zeta potential was used to measure the potential of zeolite. It was found to be negatively charged even in very acidic conditions, thus allowing the entrance of cations and not favouring the deposition of negatively charged ions into the lattice channels to make up for the positive charge deficiency.
Two isoelectric properties were studied: isoelectric point (iep) and potential determining ion. Isoelectric point (iep) is the total interaction happening at the mineral/water interface such as hydrolytic reactions, adsorption and distribution of dissolved lattice ions while potential determining ions (pdi) are ions that alters or dictates the surface charge of the material. No isoelectric point of zeolite was observed in pH between 2-12, which means that zeolites always carries a net electrical charge whatever the pH is. Increase in pH lowers the charge due to accumulation of OH\(^-\) on positively charged sites or the release of positive charges of hydroxyl groups found at the zeolite surface while decreasing the pH increases the surface charge due to adsorption of H\(^+\) onto negatively charged sites. H\(^+\) and OH\(^-\) were found to preferentially dissolve due to uneven activities present in the system, thus changing the surface charge of zeolite and dictating the mechanism of adsorption. Though a negative surface charge was obtained even when H\(^+\) ions were adsorbed at lower pH, it is possible to obtain a positive zeta potential or even reverse the zeta potential through deposition of cations with higher valence. To readily adsorb anions, the zeta potential of zeolite should be reversed [2].

Though zeolite is very good adsorbent, its properties can still be altered and modified to increase its adsorption efficiency. A study by Choi [4] specified how modified zeolite can adsorb three times better than natural zeolite. However, due to its innate negative charge, only cations have the natural affinity to be adsorbed. Nevertheless, rapid advent of previous studies show how zeolites can be a versatile adsorbent can be used to recover and isolate anions including metal complexes.

A study by K. Hor [5] implemented physicochemical methods to improve the adsorption capacity and removal efficiency of zeolites. Examples of methods used and investigated were acid treatment, base treatment, combined acid-thermal, and base thermal treatment, in which the main rationale of the treatment is to improve de-alumination and de-silication processes.

Among the modification processes that were mentioned above, manipulating the electrokinetic potential of zeolites shows the greatest promise. Electrokinetic potential or zeta potential is the electric potential in the electric double layer, at the boundary between the compact layer and diffuse layer. The boundary between the compact layer and diffuse layer is also known as the Stern layer. A key in understanding the surface properties of an adsorbent is to know its surface charge. However, surface charges are impossible to measure and instead, zeta potential is widely used to determine interaction energy between particles and colloidal stability. In adsorption processes, zeta potential measurements over a wide range of pH can be used to assess the affinity of the adsorbate ions to the surface of the adsorbent [6].

Zeolites with reversed zeta potential were able to adsorb anions, but only in small amounts and the adsorption capacity for different anions can be improved with more positive zeta potentials. One way to reverse the zeta potential of zeolites is by using CTAB (Cetyl trimethylammonium bromide) to turn natural zeolites to surfactant modified natural zeolite (SMNZ), which was studied by Barczyk [7] to allow anion sorption onto zeolite surfaces. It was found out that anion sorption of zeolite is correlated with the type anion adsorbate, type of natural zeolite, and surfactant loading level.

In this study, the Philippine natural zeolite, PNZ, will be used to adsorb gold cyanide from an anionic aqueous solution. Although zeolites have been used to adsorb anions by reversing its zeta potential, no existing researches have undertaken to study if zeolite can successfully adsorb gold cyanide. The PNZ will be modified by using CTAB to alter its zeta potential and determine whether it is efficient in adsorbing gold cyanide.

2. Experimental

2.1 Materials Preparations

The zeolite (PNZ) samples from SAILE Industries in Mangatarem, Pangasinan were selected for this study. The same PNZ sample sourced and analysed by previous researchers [8-10] was determined to be chiefly clinoptilolite. The PNZ were sieved to a particle size of 1.68 mm < Dp < 2.0 mm and washed with deionized water for four times, then dried in an oven at 150°C for three hours. The
surfactant CTAB (N-Cetyl-N, N, N trimethyl ammonium bromide) with 99% purity (sourced from Belman Laboratories) was used for the surface modification PNZ.

2.2 Sodium activation
The PNZ was soaked in 4 M NaCl solution 24 hours at a weight/volume ratio of 20% (5g dried PNZ to 25 mL NaCl solution) without agitation. After 24 hours, Na-PNZ was rinsed eight times with deionized water, and dried in an oven for 3 hours at a temperature of 150 C.

2.3 Surface Modification
CTAB was used to modify the Na-PNZ in an amount equivalent to 100% and 200% ECEC of each of the zeolites [7]. From literature [11], the computed ECEC of clinoptilolite by using the method proposed by Ming and Dixon [11] was computed to be 10 mmol/100g. Surface modification was then carried out by a ratio of five grams zeolite per 100 mL of CTAB solution with CTAB concentrations equal to both 100% and 200% ECEC of zeolites. The solutions were bottle rolled for 24 hours at 200 rpm. The suspensions were then rinsed four times with deionized water and dried in an oven for three hours at 105C.

2.4 Characterizations
The morphology of PNZ, SMNZ at 100% and 200% CEC was examined by field emission scanning electron microscopy (Fe-SEM, S-3400N, Hitachi). To further confirm if CTAB was attached on the zeolite surface, FTIR analyses were performed on an ATR-FTIR spectrometer (IS50, Thermo Scientific Nicolet) for PNZ, SMNZs at 100% and 200% CEC. The surface charge of the materials was then measured using the Zeta Meter 4.0.

3. Results and discussion
To characterize the functionality of the modified adsorbents, the Fourier-Transform Infrared Spectroscopy (FTIR) was used to determine the presence of CTAB onto the materials was determined by analysing the spectra of the materials using the scanning electron microscopy (SEM), and Zeta Potential test were performed on the materials namely PNZ, SMNZs at 100% and 200% CEC.

3.1 Functionality of PNZ and SM-PNZ
Figure 6 shows the absorbance vs wavenumber curve derived from the FTIR results. The figure shows that CTAB modification was achieved at dosages equal to 100% ECEC and 200% ECEC of the natural zeolite [12]. The presence of the CTAB modifier was observed in the spectra peaks at wavenumber 2000-2500 cm⁻¹. The observed spectra correspond to the carbon tails present in the CTAB. Also, the peak at 3300-3600 cm⁻¹ observed in the PNZ material was not seen in the spectra of SM-PNZ (100% and 200% ECEC) samples. Originally zeolites are hydrophilic due to its tetrahedral aluminosilicate network, but became hydrophobic at the presence of CTAB, which is a known surfactant. Lastly, peaks observed at 500-1300 cm⁻¹ were all observed in all FTIR spectra, which signifies that the Si-O-Si and Si-O-Al bonds were not changed upon modification.

3.2 Morphology of the PNZ and modified SM-PNZ
The images obtained by using SEM shows that the PNZ has an irregular platy-like surface morphology. Void spaces represent pores and cavities on the PNZ surface. In comparison with the SEM images of PNZ and SMNZ, faded parts are seen on some particles which signify that an organic layer has formed aggregates over the plate like morphologies of PNZ. The organic layer is assumed to be CTAB accumulated onto the PNZ external surface. More aggregates of the organic material are observed in SM-PNZ (200%).
Figure 1. FTIR Curve (a) untreated PNZ, (b) SM-PNZ (100%), and (c) SM-PNZ (200%)

Figure 2. SEM Images of (a) NZ, (b) 100%, and (c) 200% ECEC

3.3 Zeta-potential of PNZ and SMNZ

Table 1. Zeta potential of PNZ 100%, and 200% ECEC

| Adsorbent         | Zeta potential (mV, +/- 2.00 mV) |
|-------------------|----------------------------------|
|                   | pH 10   | pH 11.5  |
| PNZ               | -37.50  | 40.00    |
| SM-PNZ (100%)     | -16.20  | 25.00    |
| SM-PNZ (200%)     | -16.20  | 16.80    |
The zeta potential values of PNZ, SM-PNZ (100%) and SM-PNZ (200%) are compared. Although the zeta potential values weren’t reversed, it can be compared that the zeta potential values are close to the zeta potential of activated carbon (20-40% difference) [13]. A 100% decrease in zeta potential was observed from NZ to SM-PNZ samples which signifies that the PNZ was successfully surface modified using CTAB. This then resulted to a surface charge which is less negative than the unmodified material, PNZ.

3.4 Recovery performance of the adsorbents
The efficacy of the adsorbents, PNZ, SM-PNZ (100) and SM-PNZ (200) for the recovery of gold cyanide solution are compared and shown at Fig 3. At three (3) hours contact time, the SM-PNZ (100) has the highest % recovery. The recovery of gold cyanide almost doubled when PNZ was surface modified with CTAB. This means that surface modification is important for the adsorption of gold cyanide. However, comparing modified SM-PNZ, the recovery of gold cyanide is greater in SM-PNZ (100) than in SM-PNZ (200). This can be attributed to the fact that more aggregates of CTAB were formed on the surface of the zeolite SM-PNZ (200) making less polar than SM-PNZ (100). Thus, the external surface of SM-PNZ (200) is less attracted to anionic forms of the gold cyanide solution.

![Figure 3. Percent recovery of PNZ, SM-PNZ (100%) and SM-PNZ (200%)](image)

4. Conclusion
Results from the experiment show that zeolite has a potential in adsorbing gold cyanide ions in an anionic solution. Based from the recovery as a function of time, it indicates that in the long run, zeolites either modified or not has the same adsorption % recovery. Although the zeta potential of zeolite was not reversed in modification, the presence of CTAB molecules attached at the zeolite surface and pores may have amplified and assisted in diffusion of gold cyanide into pores and voids present in zeolite.

The study shows that PNZ can be used to treat gold cyanide wastewater from mine operations. Knowing that AC and SMNZ have close % recovery values, much research can be undertaken to manipulate zeolite such as using other modifiers or increasing the dosage of surfactants to increase its
adsorption rate and if possible, obtain higher % recovery than that attained by activated carbon. Another recommendation would be studies on how to increase the rate of adsorption, since the kinetics of this process is relatively slow compared to activated carbon.

Acknowledgment
The contribution of SAILE Industries, Inc. for the zeolite materials and technical data provided in this study is thus acknowledged. The faculty and staff of the Pilot Plant of the Department of Mining, Metallurgical and Materials Engineering is also recognised for their assistance and guidance to our study. The authors would like to extend their deepest gratitude to Dr. Ronald T. Dy for the financial support.

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