Adsorption uptake of Philippine natural zeolite for Zn\textsuperscript{2+} ions in aqueous solution

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Abstract. The Philippine natural zeolite (PNZ) was characterized and subjected to Zn\textsuperscript{2+} adsorption tests in aqueous solutions to determine its adsorption uptake and to understand its adsorption behaviour. The PNZ was characterized using XRD, SEM, BET-analysis and TG-DTA. XRD showed significant peaks indexed to natural mordenite-type zeolite along with other natural zeolites and minerals. SEM micrographs revealed a rough and corrugated surface morphology of the sample. BET physisorption analysis showed a surface area of 222.63 m\textsuperscript{2}/g. From the analytical tests report given by the supplier, the Si/Al ratio (SAR) was computed to be equal to 4.29 based on the silica and alumina content of the PNZ. Adsorption kinetic and thermodynamic studies were done to determine the adsorption mechanism and adsorption capacity of PNZ for Zn\textsuperscript{2+} ions in aqueous solution. From the adsorption kinetic curve, the PNZ attained chemical equilibrium after 50 min. Pseudo-second-order kinetic model was the most applicable kinetic model providing the highest correlation with the data. Langmuir model better described the adsorption isotherm of the PNZ than Freundlich model. The theoretical maximum cation exchange capacity of PNZ was computed as 27.17 mg Zn\textsuperscript{2+}/g according to the Langmuir model.

1. Introduction
Adsorption is a widely used technique in the treatment of waters contaminated with heavy metals due to its efficiency and practicality in industrial scale applications because it uses low energy and the operation is simple. The high-production cost of conventional sorbents makes it impractical for industrial use. Thus, the search for cost-effective adsorbents is important. Various materials have been studied in removing heavy metals including agricultural, industrial and household wastes [1], sea and ore materials, metal oxides and metal hydroxides [2], aluminosilicates and clays [3].

Being a cheap and abundant mineral, natural zeolites have already established a good reputation in heavy metal adsorption [4]. Most studies focus on the utilization of natural zeolites found in different places [4-7]. The determination of the adsorption capacities and the understanding of the adsorption kinetics and adsorption isotherms for different heavy metals in aqueous environment are the typical
outcomes reported in various literatures. There are also studies on various modification or activation techniques through the use of chemicals to improve their sorption [7]. Natural zeolite contains varying amount of certain types of zeolites which have different adsorption properties. This makes it necessary to test all existing natural zeolites for heavy metal adsorption due to compositional variations in different locations.

Philippine natural zeolite (PNZ) was found to have great potential in adsorbing heavy metals like arsenic, As$^{3+}$, zinc, Zn$^{2+}$, and chromium, Cr$^{6+}$ as recently reported [8, 9]. Several aspects were not addressed in these works especially the kinetic adsorption behavior and thermodynamic isotherm of the material.

In this study, the PNZ is characterized for its mineralogy, texture and morphology, surface area, chemical components, and Si/Al ratio (SAR). Batch adsorption experiments were done to determine the feasibility of the material for sorption of heavy metals in aqueous solutions as represented by zinc (Zn$^{2+}$) ions. Adsorption kinetic study was done to understand its adsorption mechanism while kinetic study was conducted to determine its maximum adsorption capacity.

2. Experimental Methods

2.1. Material Characterization

The PNZ (Saile Zeolite Aqua Grade) was supplied by SAILE Industries, Inc. The mineral was mined in Mangatarem, Pangasinan, Philippines. It was ground using mortar and pestle and filtered using a 200 mesh sieve. Then the material was washed with deionized water and dried at 105°C for 24h. No additional treatment was done prior to characterization and adsorption tests.

The PNZ were analyzed using an X-ray diffractometer (SHIMADZU, XRD-7000 Maxima) with Cu Ka (1.5406 Å) radiation to check their composition and/or crystal structure. Continuous scan was conducted, typically from 3.00 up to 90.00° with a speed of 2.00°/min. Scanning electron microscopy (JEOL, JSM 6010LV) was performed to observed the surface texture and morphology of the sample. Brunauer-Emmett-Teller (BET) physisorption analysis was conducted to measure the surface area.

2.2. Adsorption kinetics and thermodynamics study

The Zn$^{2+}$ ion adsorption of PNZ through time was investigated in the kinetic study. Stock of feed solution with a concentration of 600 mg Zn$^{2+}$/L was prepared by dissolving 0.51 g of zinc acetate dihydrate [C$_{4}$H$_{4}$O$_{4}$Zn·2H$_{2}$O, Sigma-Aldrich, ≥ 98%] with 250 mL deionized water. The stock solution was acidified by adding 3 mL of glacial acetic acid [CH$_{3}$COOH, J.T. Baker, assay 100%] to reduce possible adsorption of Zn$^{2+}$ ions by the glass container. For every experiment, the stock solution was diluted to produce feed solution with 100 mg Zn$^{2+}$/L concentration. Then, 0.25 g of adsorbent was added to 100 mL of the prepared feed solution and stirred magnetically at 100 rpm under room temperature. Certain volume (~10 mL) was subsequently removed at various times: 0, 10, 30, 60, 90, 120, 150,180 min, after the initial contact. A minute before each removal, the mixture was agitated by increasing the magnitude of stirring to 500 rpm to ensure uniform distribution of adsorbent. The stirring was brought back immediately to 100 rpm after each removal. The samples were centrifuged for 5 min and filtered using a Nylon syringe filter (0.45 µm pore size, 25mm diameter) to separate the adsorbent from the supernatant. The concentration of Zn$^{2+}$ in the supernatant was measured using SHIMADZU AA-7000 Atomic Adsorption Spectrometer. Calibration was performed before every use of the instrument by measuring solutions of known concentration to produce a calibration curve.

In the thermodynamic study, feed solutions with various initial concentrations (10, 25, 50, 100, 200 and 400 mg Zn$^{2+}$/L, pH = 6) were prepared by dissolving corresponding amount of zinc acetate dihydrate to 500 mL of deionized water. The pH was controlled by dropping 0.1M of NaOH or 1.0M of glacial acetic acid. Again, for every 100 mL of feed solution, 0.25 g of adsorbent was added. The mixture was magnetically stirred at room temperature at 100 rpm for 180 min to attain chemical equilibrium. The samples were centrifuged and the supernatant was collected with the use of nylon syringe filter.

The adsorbed amount of Zn$^{2+}$ ions is evaluated using the equation,
where $C_0$ is the initial zinc ion concentration (mg Zn$^{2+}$/L), $C_i$ is the concentration (mg Zn$^{2+}$/L) of the supernatant after some time $i$, $V$ is the batch volume (L), and $m$ is the adsorbent mass (g).

2.3. Kinetic model construction and evaluation of the goodness-of-fit

The adsorption through time is studied. Three kinetic models were taken into consideration to describe the kinetic adsorption behaviour: pseudo-first-order kinetic model [10], pseudo-second-order kinetic model [11], and intra-particle diffusion model [7, 12]. For the thermodynamics study, the adsorption capacity at different initial feed solution concentrations was firstly determined. The adsorption isotherm, variation in the equilibrium adsorption capacity with the equilibrium Zn$^{2+}$ ion concentration, was modelled using Langmuir [13] and Freundlich models [14].

The various parameters and constants of different models are determined by i) plotting the experimental data according to the linear form of the different models, ii) followed by choosing the best fit line, and lastly iii) by computing the desired constants for each model based on the value of the slope and y-intercept of the best-fit line. The best model is selected according to the values of the $R^2$. The nearer the value of $R^2$ to 1, the better the fit.

3. Results and Discussion

3.1. Structure and crystallinity

The PNZ is composed mainly of mordenite, clinoptilolite and chabazite as shown in its diffractogram in figure 1. The peaks from Na-type mordenite (amscd 0003444) [15], Ca-type clinoptilolite (amscd 0001304) [16], Ca-type chabazite (amscd 0017693) [17], Ca-type heulandite (amscd 0000180) [18] as well as calcite and quartz were indexed via manual matching. However, the amount of each mineral is difficult to ascertain from the diffractogram.

3.2. Surface texture, morphology and surface area

The powder particles of the PNZ, as it appears in figure 2, have rough and corrugated surface, which is favourable since water molecules could infiltrate the zeolite matrix more efficiently. Due to the wide particle size distribution of the particles, no average size can be obtained. But most particles are less than 50 μm.

PNZ has a very high surface area of 222.63 m$^2$/g as computed from the BET physisorption analysis. Surface area is an important property of every adsorbent. Theoretically, the higher the surface area, the greater the potential sites available for the adsorption of heavy metal ions. This is especially true when there is only a single layer active in the adsorption or when physisorption is considered.

![Figure 1. XRD pattern of the Philippine natural zeolite.](image-url)
3.3. Si/Al ratio (SAR)
According to the analytical test report provided by the supplier, the PNZ contains various compounds like silica, alumina, ferric oxide, and lime. Table 1 shows the corresponding weight percentages of each compound. The major components are silica, alumina and lime which make up 57.42, 11.36 and 4.46 % respectively. It should be noted that only 57.42% of the total weight of the natural zeolite is attributed to SiO$_2$ while 11.36% of the weight is credited to Al$_2$O$_3$, which suggests that the total zeolite content of PNZ is around 68.78% of its total mass.

The computed Si/Al ratio (SAR) based on chemical analysis report was 4.29. Take note that it does not necessarily represent the actual SAR of the mordenite nor the other zeolite materials since the mineral is a combination of various aluminosilicates (i.e. clinoptilolite, mordenite, chabazite, quartz).

3.4. Kinetic study
Figure 3 shows the best fit lines generated from the linearized form of the kinetic adsorption data according to the different kinetic models. Also, included are the resulting plots of the three models. The comparison of the experimental and computed values of the adsorption capacities $q_e$ are shown in table 2 together with the computed coefficients of the three kinetic models. There is a small difference between the computed adsorption capacities of the pseudo-first-order and pseudo-second-order kinetic models wherein the former has a value closer to the experimental data. However, the best kinetic model does not rely on this aspect alone. Considering $R^2$ values, the pseudo-second-order offers the best fit curve since it gives the value nearest to 1 among the three models. Intra-particle diffusion kinetic model commonly generates positive errors. Undoubtedly, the kinetic behaviour follows pseudo-second-order kinetic model. Similarly, Wang et.al found that pseudo-second order provided the best model in describing the adsorption of Ni$^{2+}$ ions onto natural Na-mordenite zeolites [19]. Pseudo-second-order model is based on a chemisorption adsorption mechanism [11]. Cation exchange is therefore applicable for this case.

Table 1. Chemical composition of the Philippine natural zeolite.

| Compound  | SiO$_2$ | Al$_2$O$_3$ | CaO | Fe$_2$O$_3$ | Ca | MgO | Na$_2$O | K$_2$O | H$_2$O | LOI$^b$ |
|-----------|--------|-------------|-----|-------------|----|-----|--------|--------|--------|--------|
| Weight (%)| 57.42  | 11.36       | 4.46| 3.72        | 3.19| 1.40| 0.87   | 0.053  | 9.99   | 10.49  |

$^a$ Computed from Fe$^{3+}$
$^b$ Loss on Ignition
3.5. Thermodynamic study

Figure 4 presents the best fit lines of the linearized form of the equilibrium data based on Langmuir and Freundlich models. The resulting thermodynamic isotherms were also shown. The corresponding coefficients of each model are listed in table 3. Langmuir model fits better to the adsorption data than Freundlich since the $R^2$ value generated from the former (0.99) is higher compared to the latter (0.92). Langmuir model assumes an uptake that occurs on a homogeneous surface by monolayer sorption in the absence of interaction between molecules [20]. The equilibrium parameter $R_L$ is equal to 0.3581 for the PNZ, which is within the range from 0 to 1, implying a favourable type of adsorption.

Comparatively, Nakamoto et.al observed that the thermodynamic adsorption isotherm of mordenite for Pd$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Ni$^{2+}$ was best described by Langmuir model [21]. The same model also gave the best fit as Wang et.al reported for the adsorption of Ni$^{2+}$ by natural Na-mordenite at temperatures 30 and 40°C [19]. Accordingly, the adsorption was also of favourable type.

The experimental adsorption of PNZ is 16.17 mg Zn$^{2+}$/g while the Langmuir computes a maximum adsorption capacity of 27.17 mg Zn$^{2+}$/g. The gap was probably brought by the highest Zn$^{2+}$ ion concentration of the feed solution in the thermodynamic study which, perhaps, not high enough to saturate or completely enclose the PNZ with a monolayer of adsorbate.

The adsorption capacities of selected low-cost sorbents are presented in table 4. Natural zeolites with high amount of mordenites tend to have better adsorption than PNZ. This is because mordenite-type zeolites have high CEC which is equal to 2.29 meq/g [5]. Although PNZ contains significant...
amount of mordenite, clinoptilolite, and chabazite, it also contains other materials that do not necessarily adsorbed heavy metal cations or have low sorption. Moreover, the ability to exchange cations might have been affected by natural cations (i.e. Fe ions) present on the mining site which already ‘filled’ the zeolites’ active sites.

Given the relatively higher maximum adsorption capacity of PNZ, the material can be a good alternative for the removal of heavy metals in contaminated waters. Though some materials like the
modified orange peel has greater potential in wastewater treatment, their biodegradability makes it unfavourable for long-term use.

Activated materials make better uptake performance. Therefore, the adsorption capacity of PNZ can still be improved upon modification through chemical (i.e. HCl, NaOH, HNO₃, ion-exchange, etc.) or physical means (i.e. plasma modification, irradiation).

4. Conclusions

Philippine natural zeolite was found to have mordenite as its major base component along with other phases (i.e. clinoptilolite and chabazite) and impurities such as quartz and calcite. According to chemical analysis provided by the supplier, the material is made up of around 68.78 % zeolite relative to its total mass. The Si/Al ratio is computed to be equal to 4.29. The material is made up of particles with rough and corrugated surfaces and sizes of less than 50 μm. Physisorption analysis showed a surface area of 222.63 m²/g. Considering these characteristics, the adsorption behavior was investigated through adsorption experiments. Among pseudo-first-order, pseudo-second-order, and intra-particle diffusion model, the pseudo-second-order kinetic model was found to be the most suitable in representing the kinetic adsorption data. The results suggest that cation exchange is the most dominant sorption mechanism for PNZ. From the thermodynamic study, Langmuir model provides better fit than Freundlich model. Accordingly, the theoretical maximum adsorption capacity was found to be equal to 27.17 mg Zn²⁺/g. In comparison with other sorbents, PNZ has relatively high adsorption capacity. The material has a very high potential for heavy metal sorption of contaminated waters.

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