Application of zeolite intercalated calcium carbonate from pokea shell (Batissa violacea celebensis) waste as adsorbent Ni\(^{2+}\) ion

Mashuni\(^*\), L O Ahmad\(^1\), F H Hamid\(^1\), Sudarlin\(^1\)

\(^1\)Department of Chemistry, Faculty of Mathematics and Natural Sciences, Halu Oleo University, Kendari, Southeast Sulawesi

*Email: mashuni2696@gmail.com

Abstract. The purpose of this study was to obtain adsorbent zeolite modified by CaCO\(_3\) from pokea shell (PS) waste to adsorb Ni\(^{2+}\) ions. Adsorbents are made through the intercalation method, where the PS powder is mixed to zeolites in 0.1 M HCl with 3 ratios of 3:1, 2:2 and 1:3 (g/g), respectively. The optimization of adsorption power was carried out by using parameters such as pH, contact time and concentration variation of Ni\(^{2+}\) ion solution. The analysis of the adsorption capacity and type of bond using the Freundlich and Langmuir isotherm equations. The characterization of the active site composition of the adsorbent was used FTIR instrument. FTIR spectra showed that CaCO\(_3\) modified zeolite adsorbent include Si-OH, O-H, Al-O, Si-O, C-H, Ca-C and C-O from CaCO\(_3\) and C-O from CO\(_3\)\(^2-\) functional groups. The results showed that the best adsorbent was it with the zeolite-PS powder ratio of 3:1, the optimum conditions were obtained at pH 5, contact time at 60 minutes and 45 mg l\(^{-1}\) concentration. Adsorption of Ni\(^{2+}\) ions meets the Freundlich isothermal with adsorption capacity and energy of 1.33 mg g\(^{-1}\) and 5.78 kJ mol\(^{-1}\).

1. Introduction
Technological advances can have a positive impact, including the welfare of the community. Apart from having a positive impact, negatively impacts the form of environmental damage due to the disposal of heavy metal waste without prior processing. Heavy metals can cause pollution impacts on aquatic ecosystems leading to a decrease in water quality due to the properties of heavy metals that are undegradable and easily absorbed [1]. One of the most dangerous heavy metals is nickel. Nickel is a heavy metal that is very dangerous to human health and is toxic and disrupts environmental sustainability. Several chemical methods have been attempted to remove heavy metals, including adsorption, ion exchange and membrane separation. The adsorption process is more widely used in industry because it is more economical and does not cause toxic side effects [2].

One of the potential adsorbents to be used is zeolite. Zeolite has advantages when compared to other adsorbents. Natural zeolite adsorption work is generally lower than synthetic zeolite [3], so that to increase its adsorption capacity, the character of the zeolite surface needs to be changed by carrying out a surface modification process through various methods including zeolite activation. Zeolite surface activation is a method to remove impurities and open zeolite pores so that its ability as an adsorbent can be optimized. Besides, another method that can be done is intercalation modification. Mazur et al. (2014) [4], define interaction as the insertion of species in the space between layers of solids while maintaining
the layered structure. The atoms or molecules inserted are called intercalates, while those that are the places where the atoms or molecules will be inserted are called intercalates. This method will enlarge the pores of the material because intercalation will push the layers or open between layers to expand. One of the ingredients that can be added is calcium carbonate (CaCO$_3$) from the pokea shell (PS). The addition of CaCO$_3$ aims to stretch the layer spacing on the zeolite so that its adsorption capacity can increase. The increase in zeolite adsorption power is expected to save the use of zeolite as an adsorbent. PS (Batissa violacea celebensis), which are widely distributed in Pohara and Wanggu, Southeast Sulawesi.

PS is a type of mollusc found in the inland waters of Southeast Sulawesi and included in the bivalve class (two shells). PS is rich in CaCO$_3$, around 98.5% [5]. PS is often considered a waste when the contents of PS have been consumed, even though the PS contains very high CaCO$_3$. The CaCO$_3$ can be used as a filler in zeolites. Pratomo et al. (2017) [2], used the active zeolite adsorbent to adsorb Cd$^{2+}$ metal ions, the adsorption capacity was 2.01 mg g$^{-1}$. Raziah et al. (2017) [6], adsorption of metal ion Cd$^{2+}$ using natural zeolite obtained an adsorption capacity of 0.082 mg g$^{-1}$. The research Putri and Sabani (2018) [7], adsorption of Mg using active zeolite obtained the absorption percentage of 99.99%. The results of these studies indicate that natural zeolite and PS waste can be further processed as adsorbents and are expected to increase their added value. Based on the description above, this research will use the intercalated active natural zeolite with CaCO$_3$ from PS waste as an adsorbent to overcome Ni$^{2+}$ ion pollution.

2. Materials and Methods
2.1. Materials
PS dried and smoothed to 250 mesh size. Natural zeolite (250 mesh), 1000 mg l$^{-1}$ nickel (Ni$^{2+}$) solution made in various concentrations, i.e. 0; 0.2; 0.4; 0.6; 0.8 dan 1 mg l$^{-1}$ (1% HNO$_3$ as a solvent) for standard solutions, 37% HCl and 0.1 M NaOH.

2.2. Zeolite Activation
Zeolite is activated by two methods, namely chemical methods and physical methods (thermal/heating). In the chemical method, 40 g of zeolite is activated by immersing in 50 ml of 1 M HCl for 24 hours, then filtered and rinsed with distilled water and heated for 3 hours at 105°C. Furthermore, the thermal method is by heating (calcination) the zeolite at 300°C for 3 hours [8]. The activated zeolite (AZ) characterization used FTIR.

2.3. Zeolite Intercalation
The AZ and PS powder that had been prepared were mixed in a ratio of 3:1, 2:2 and 1:3. The AZ and PS were mixed with 25 ml of 0.1 M HCl and allowed to stand for 24 hours. The mixture was filtered and the precipitate was rinsed with distilled water until it reached a neutral pH, then dried in an oven at 105°C for 2 hours [9]. Characterization of zeolite-CaCO$_3$ using FTIR.

2.4. Ni$^{2+}$ Ion Adsorption
Adsorption of Ni$^{2+}$ ions was analyzed with a variety of treatments, including (1) the effect of intercalated zeolite-CaCO$_3$ adsorbent 3:1, 2:2 and 1:3 with a solution of ion Ni$^{2+}$ 5 mg l$^{-1}$ (pH 5), (2) The effect pH of Ni$^{2+}$ ion with the variation of pH 3, 4, 5, 6, and 7 with intercalated zeolite-CaCO$_3$ absorbent 3:1, (3) The effect contact time of 15, 30, 60, 90 and 120 min, (4) The effect of the concentration of Ni$^{2+}$ ions with the concentration of 5, 15, 30, 45 and 60 mg l$^{-1}$. Adsorption was carried out each with a ratio of 1:50 (w/v) and the solution was shaken at a speed of 175 rpm. The filtrate was separated and analyzed using an AAS instrument to determine the concentration of metal ions that were not adsorbed by the adsorbent.

3. Results and Discussion
Zeolite activation aims to increase the adsorption capacity of natural zeolites by chemical and physical
means. Chemical activation by washing natural zeolites from impurities such as organic compounds that still cover the active sites of natural zeolites, which is immersed in a strong acid solution which can dissolve and remove absorbed metal oxides and cover the zeolite surface so that it is more porous and the surface of the contact plane becomes larger [10]. Meanwhile, physical activation by calcination aims to remove or evaporate impurities that remain on the surface of the adsorbent so that active sites can appear. In this research, the CaCO$_3$ intercalation technique from the PS was carried out. A material that is good enough to be used as an intercalation material is natural zeolite, where the structure between the zeolite layers is easily modified so that when intercalated, the space between layers of natural zeolite will increase so that the metal ions are easier to enter and bond.

3.1. Characterization of activated zeolite and zeolite-CaCO$_3$ by FTIR

![Figure 1. FTIR](image)

**Figure 1.** FTIR (a) activated zeolite, (b) zeolite-CaCO$_3$ 3:1, (c) zeolite-CaCO$_3$ 2:2, (d) zeolite-CaCO$_3$ 1:3

**Table 1.** Functional groups of AZ and zeolite-CaCO$_3$

| Functional groups | AZ       | Zeolite-CaCO$_3$ 3:1 | Zeolite-CaCO$_3$ 2:2 | Zeolite-CaCO$_3$ 1:3 | References [11-13] |
|------------------|----------|---------------------|---------------------|---------------------|------------------|
| O-H              | 3444.87  | 3444.87             | 3446.87             | 3441.01             | 3643-3433        |
| C-H              | 2918.30  | 2918.30             | 2918.30             | 2918.30             | 2854-2924        |
| O-H              | 2850.79  | 2850.79             | 2850.79             | 2850.79             | 2854-2851        |
| C-O              | 2357.01  | 2360.87             | 2360.87             | 2357.01             | 2368-1080        |
| O-H              | 1647.21  | 1645.25             | 1647.21             | 1647.21             | 1655-1635        |
| Si-O and Al-O    | 1043.49  | 1041.56             | 1035.77             | 1072-1040           |                  |
| Ca-C and C-O     | 860.25   | 860.25              | 860.25              | 860.25              | 862-856          |
| Si-C             | 835.18   | -                   | -                   | -                   | 890-690          |
| Al-O-Al          | 796.60   | 794.67              | 794.67              | 794.67              | 795-750          |
| Si-O-Si          | 545.45   | -                   | -                   | -                   | 550-470          |

Figure 1. shows that the zeolite from the Pokéa shell has been perfectly intercalated because there has been a shift in the wavenumber before it is intercalated and after it has been intercalated, namely the O-H bending vibration of silanol there is a shift in the wavenumber from 1647.21 cm$^{-1}$ to 1645.25 cm$^{-1}$ which indicates absorption. The O-H from silanol is getting sharper and stronger. In the bending
vibration of Al-O-Al, there is a shift in the wavenumber from 796.60 cm\(^{-1}\) to 794.67 cm\(^{-1}\) which indicates that the absorption of Al-O-Al is getting sharper and stronger (spectrum b). Likewise, in spectrum c and d, there is a shift in wavenumbers, but not too strong and sharp. Before intercalation, it only has a few active groups, but after intercalation, it has many additional active groups including the absorption band at wavenumber 2918.30 cm\(^{-1}\) which indicates the C-H strain vibration, the O-H strain vibration absorption band is shown at wavenumber 2850.79 cm\(^{-1}\), the absorption band at wavenumber 860.25 cm\(^{-1}\) which indicates a vibration of Ca-C and C-O bending from CaCO\(_3\) and the absorption band at a wavelength of 2357.01 cm\(^{-1}\) which indicates that there is a CO group from CO\(_3^{2-}\).

The occurrence of intercalation can be observed from a shift in the vibration spectrum towards a higher wavenumber [12]. Li [13], researched by including TiO\(_2\) on zeolites. The results showed that the absorption band in the area between the AZ and the zeolite that had been intercalated with TiO\(_2\) showed that the wavenumber 3610 cm\(^{-1}\) (O-H bending vibration), between pure zeolite and zeolite-TiO\(_2\) became narrower due to the shift of TiO\(_2\) against OH. This study is based on the results of FTIR characterization that the best zeolite-CaCO\(_3\)) is at a ratio of 3:1 due to a narrowing of the spectrum band, a shift in higher wavenumber and the emergence of new functional groups, while in the adsorbent the ratio of 2:2 and 1:3 only occurs a shift in higher wavenumber and the emergence of new functional groups.

### 3.2. The Ni\(^{2+}\) Ion Adsorption

![Figure 2](image)

*Figure 2.* (a) The effect of adsorbent, (b) The effect of pH, (c) The effect of contact time, and (d) The effect of Ni\(^{2+}\) ion concentration

Figure 2, showed that the adsorption efficiency of Ni\(^{2+}\) ions increased in the adsorbent ratio 3:1 compared to the ratio 2:2 and 1:3. It is because at a ratio of 3: many active groups can absorb Ni\(^{2+}\) ions and possibly a larger pore surface area. Figure 2(b) showed that the maximum absorption of Ni\(^{2+}\) ion by zeolite-CaCO\(_3\) adsorbent occurs at pH 5, namely 0.1041 mg g\(^{-1}\). However, there was a decrease in adsorption at pH 6 and 7, indicating that there has been precipitation in the solution. The adsorbent molecules are chemically considered to have active sites or functional groups capable of interacting with metals. If the adsorption process is through ion exchange, the adsorption is influenced by the number of protons in the solution that compete with metal ions on the adsorbent surface. Thus, low pH (acid),
which is below pH 5, the number of protons ($H^+$) is abundant resulting in a relatively small chance of metal binding by the adsorbent or decreased absorption efficiency [14,15]. Whereas at neutral pH, metal ions can undergo hydrolysis reaction in solution to become unstable in the form of the original metal ions, so that their absorption efficiency ability decreases [2, 11]. The research by Pratomo et al. (2017) [2] showed that the optimum pH is 5.

Figure 2(c) showed that the adsorption rate of $Ni^{2+}$ ions by zeolite-CaCO$_3$ adsorbent increased until the contact time was 60 minutes and then decreased at the contact time of 90 minutes to 120 min due to the saturation of the adsorbent surface. The longer the contact time between the adsorbent and $Ni^{2+}$ ions solution, the more will be adsorbed. However, the amount of this adsorbed substance will be maximum at a certain time, where the adsorbent is no longer able to adsorb the $Ni^{2+}$ ions solution because the surface is saturated so that the adsorption rate is reduced [2]. Figure 2(d) showed that the adsorption power of $Ni^{2+}$ ions by zeolite-CaCO$_3$ adsorbent increased with increasing concentration of $Ni^{2+}$ ions solution, but at a concentration of 60 mg.l$^{-1}$, the adsorption power decreased. It is because, at this concentration, the active site of the adsorbent is saturated. After all, the surface has been filled with $Ni^{2+}$ ions and is unable to bind the $Ni^{2+}$ ions, whose levels are still quite a lot in the solution. [2, 16]. Langmuir adsorption theory [15, 17], states that on the adsorbent surface, there are several active sites which are proportional to the surface area of the adsorbent, where each active site can only adsorb one molecule. When the active site of the adsorbent has not been saturated with $Ni^{2+}$ ions solution, the increase in solution concentration will increase the amount of solution linearily. Then, if the active site of the adsorbent is saturated with the solution, increasing the solution concentration will not increase the amount of solution.

3.3. Adsorption isotherm

The adsorption process between the adsorbent and $Ni^{2+}$ ion solution can occur physically or chemically. The adsorption isotherm can determine the type of adsorption that occurs qualitatively where the adsorption results are plotted on the linearity curve. In general, for solid-liquid system adsorption, two types of isothermal equations apply, namely Freundlich adsorption and Langmuir adsorption. The parameter used for selecting the type of adsorption isotherm is the degree of linearity, which is determined by the linear regression value ($R^2$) [18]. The isothermal graph of Freundlich and Langmuir $Ni^{2+}$ ion by zeolite-CaCO$_3$ adsorbent respectively is presented in Figure 3.

![Figure 3](image_url)

**Figure 3.** (a) Freundlich isothermal dan (b) Langmuir isothermal

Figure 3(a) and 3(b). The correlation factor ($R^2$) for the Freundlich equation is 1, and the Langmuir is 0.867. The adsorption type of metal ion $Ni^{2+}$ by zeolite-CaCO$_3$ is Freundlich isothermal, where the adsorption occurs physically by many layers. Physisorption is adsorption that involves intermolecular forces (Van der Waals bond), and the bond is weak because there is no electron transfer [19, 20]. However, it does not rule out that there are also active groups that can bind $Ni^{2+}$ metal ions and are absorbed in the adsorbent pores, in other words, chemical bonding or electron transfer occurs, as shown in Figure 2c that after the optimum time a desorption process occurs which is not too large. It allows a
chemical bond between the adsorbent group and the Ni$^{2+}$ ion. Freundlich isothermal equation is based on the formation of layers of adsorbate molecules on the adsorbent surface that relates the amount of adsorbed substance to the number of substances remaining in solution. From calculations using the Freundlich equation, the adsorption capacity ($K_F$) is 1.33 mg g$^{-1}$, and the adsorption energy is 5.78 kJ mol$^{-1}$. Physical adsorption occurs when the adsorption energy is less than 20 kJ mol$^{-1}$ [21].

The adsorption capacity value indicates that zeolite-CaCO$_3$ can adsorb the Ni$^{2+}$ ions by 1.33 mg g$^{-1}$. This value is greater than the adsorption process of PS powder polarized clay in adsorbing Ni$^{2+}$ ions of 0.4819 mg g$^{-1}$. The research Raziah et al. (2017) [6], adsorption of metal ion cadmium using natural zeolite, obtained an adsorption capacity of 0.082 mg g$^{-1}$. It indicates that the intercalation process was successful in which the zeolite-CaCO$_3$ adsorption capacity was greater than that which was not intercalated.

4. Conclusion
The present study has focused on the interface effect between the natural zeolite and CaCO$_3$ from PS on the intercalate activity of zeolite-CaCO$_3$. FTIR analysis showed that there was intercalation between zeolite and CaCO$_3$. The best treatment of zeolite-CaCO$_3$ adsorbent is 3:1 with an adsorption power of 0.1041 mg g$^{-1}$, optimal pH of adsorption is 5, adsorption contact time is 60 minutes, and optimal adsorption concentration of 45 mg l$^{-1}$. The adsorption capacity for the zeolite-CaCO$_3$ adsorbent is 1.33 mg g$^{-1}$, and the adsorption energy is 5.78 kJ mol$^{-1}$ with the type of adsorption following the Freundlich isothermal, which shows that the adsorption process occurs physically.

References
[1] Wali W, Emiyarti and Afu L O A 2020 Sapa Laut 5 27-47
[2] Pratomo S W, Widhi M F and Triastuti S 2017 Indonesian Journal of Chemical Science 6 161-167
[3] Zuo S, Jing Z, Tao M, Tao Z and Wang Y 2019 Appl. Chem. Ind. 48 1136-1145
[4] Mazur M, Eliasova P C, Roth W J and Cejka J 2014 Catalysis Today 227 37-44
[5] Rasyid S A, Bintang M, Priosoeryanto B P, Nurlila R U and Surya R A 2018 Indian Journal of Public Health Research & Development 9 345-350
[6] Raziah C, Zerlinda P, Atika R L, Sofyana, Zuhra, Suhendrayatna and Sri M 2017 Jurnal Teknik Kimia USU 6 1-6
[7] Putri W K and Sabani 2018 Jurnal Einstein 6 22-28
[8] Haerunnisah W O, Rizal S, Wahyu dan Ahmad L O 2018 Peningkatan Daya Adsorpsi Zeolit Menggunakan Bahan Pengisi Kalsium Carbonat dari Limbah Cangkang Pokea (B.Violacea Celebensis) dan Penggunanannya dalam Pengolahan Limbah Deterjen “Thesis” (Kendari : Universitas Halu Oleo)
[9] Suriani 2016 Pemanfaatan Karbon Aktif dari Kulit Biji Mete dan Serbuk Cangkang Pokea untuk Adsorpsi Logam Berat Kadmiun(Cd) “Thesis” (Kendari : Universitas Halu Oleo)
[10] Ngapa Y D 2017 Jurnal Kimia dan Pendidikan Kimia 2 90-96
[11] Schulman E, Wu W and Liu D 2020 Materials 13 1-52
[12] Fitriyiah 2016 Jurnal Kimia dan Pendidikan 1 162-175
[13] Li F, Yinhshan J, Lixin Y, Zhengwen Y, Tianyi H and Shenmei S 2006 Applied Surface Science 252 1410-1416
[14] Taty-Costodes V C H, Faudet C, Porte and Delacrix A 2003 J.Hazard Mater 105 121-142
[15] Cordero B, Lodeiro P, Herrero R and Sastre de Vicente M E 2004 Environmental Chemistry 1 180-187
[16] Yuliusman dan Adelina P W 2010 Pemanfaatan Kitosan Dari Cangkang Rajungan Pada Proses Adsorpsi Logam Nikel Dari Larutan NiSO$$_4$$ “Thesis” (Depok: Universitas Indonesia)
[17] Li H, Zheng F, Wang J, Zhou J, Huang X, Chen L, Gao J, Zhen Q, Bashir S, Liu J L, Hu P 2020 Chemical Engineering Journal 390 1-11
[18] Atkins P W 1999 Kimia Fisika 2 (Jakarta: Erlangga)
[19] Susanto T 2011 *Jurnal Dinamika Penelitian Industri* **22** 41-47
[20] Amft M, Lebégue S, Eriksson O and Skorodumova N V 2011 *Journal of Physics* **23** 395001
[21] Bansal R C and Meenakshi G 2005 *Activated carbon adsorption* (New York: CRC Press)