EFFECTIVENESS OF HYDROCHLORIC ACID ACTIVATED BENTONITE IN LOCAL SALT PURIFICATION

Muslimah[*], **Puji Wahyuningsih**[*], **Yusnawati**[**]
[*]*Department of Chemistry, Faculty of Engineering, University of Samudra, Langsa, Aceh, Indonesia,*
muslimah@unsam.ac.id, puji_wahyuningsih@unsam.ac.id
[**]*Department of Industrial Engineering, Faculty of Engineering, University of Samudra, Langsa, Aceh, Indonesia, yusnawati@unsam.ac.id*

Email Correspondence : puji_wahyuningsih@unsam.ac.id

Received : October 11, 2022 Accepted : March 11, 2023 Published : June 30, 2023

Abstract: Various purification techniques have been developed to improve the quality of local salt, especially the NaCl content of more than 94%. One of the binding materials used in salt purification is bentonite. This study aims to synthesize modified bentonite using hydrochloric acid (HCl) solution and measure the metal content of NaCl, Pb, Ca, and Mg using AAS. The synthesis of activated bentonite was carried out using the hydrolysis method using 0.1 M HCl (1:10). Bentonite was separated from the filtrate and dried at 110°C for 2 hours. Bentonite, which had been activated with HCl, was dried again at 170°C for four hours. Analytical methods such as XRD, FTIR, and SEM were used to characterize HCl-activated bentonite. The results of the analysis showed that the acid activation process did not change the basal spacing d_{001} on the bentonite diffractogram. FTIR analysis showed that there was a shift in the -OH stretching vibration towards a lower wave number and a decrease in the absorption intensity. The activation process will reduce the pore size and increase the surface area and porosity of the bentonite. The results of the AAS analysis showed that the NaCl content in the salt increased after the purification process using acid-activated bentonite, followed by a decrease in the metal content of Mg. Based on the results of the analysis, it can be concluded that HCl-activated bentonite is effectively used in the salt purification process to improve salt quality.
Keywords: Bentonite; Activation; Local Salt; Purification

Abstrak: Berbagai teknik pemurnian telah dikembangkan untuk meningkatkan kualitas garam lokal, khususnya kandungan NaCl besar dari 94%. Salah satu zat pengikat yang digunakan dalam pemurnian garam adalah bentonit. Penelitian ini bertujuan untuk mensintesis bentonit termodifikasi menggunakan larutan asam klorida (HCl), dan mengukur kadar logam NaCl, Pb, Ca, dan Mg menggunakan metode SSA. Sintesis bentonit teraktivasi dilakukan menggunakan metode hidrolisis menggunakan 0,1 M HCl (1:10). Bentonit dipisahkan dari filtrat dan dikeringkan pada suhu 110°C selama 2 jam. Bentonit yang telah diaktivasi dengan HCl dikeringkan kembali pada suhu 170°C selama empat jam. Metode analisis seperti XRD, FTIR, dan SEM digunakan untuk mengkarakterisasi bentonit teraktivasi HCl. Hasil analisis menunjukkan bahwa proses aktivasi asam tidak mengubah *basal spacing* d_{001} pada difraktogram bentonit. Analisis FTIR menunjukkan terjadi pergeseran vibrasi ulur -OH ke arah bilangan gelombang yang lebih rendah dan penurunan intensitas serapan. Proses aktivasi akan memperkecil ukuran pori dan memperbesar luas permukaan serta porositas pada bentonit. Hasil

DOI: 10.22373/ekw.v9i1.15229

analisis SSA menunjukkan bahwa kandungan NaCl pada garam mengalami peningkatan setelah proses pemurnian menggunakan bentonit teraktivasi asam yang diikuti dengan penurunan kadar logam Mg. Berdasarkan hasil analisis dapat disimpulkan bahwa bentonit teraktivasi HCl efektif digunakan dalam proses pemurnian garam untuk meningkatkan kualitas garam.

Kata Kunci: Bentonit, Aktivasi, Garam Rakyat, Purifikasi

Recommended APA Citation :

Muslimah, Wahyuningsih, P., & Yusnawati. (2023). Effectiveness of Hydrochloric Acid Activated Bentonite in Local Salt Purification. *Elkawnie*, *9*(1), 71-80. https://doi.org/10.22373/ekw.v9i1.15229

Introduction

One of the main products in Indonesia is salt, which serves as a strategic commodity for both domestic and industrial needs (Widjaja *et al.*, 2019). With a total annual production of 433.85 tons of salt, East Aceh Regency is one of the salt-producing regions in Aceh Province. However, this production only meets 26% of the population's salt requirements (1,350 tons) (Annual Report of Department of Fisheries and Marine, East Aceh Regency. 2020). In addition to salt production not fulfilling the community's needs, the quality of salt still needs to improve. So, efforts are required to increase production and enhance salt quality in accordance with the Indonesian National Standard (SNI).

The findings revealed the quality parameters of common salt in East Aceh Regency, including its 10.98% NaCl content, 7% water content, 4% water-insoluble portion, and 42.49 mg/kg iodine content. From these data, the NaCl content and the part insoluble in water do not meet the SNI quality standards for NaCl content, namely, at least 94 % and the part insoluble in water is a maximum of 0.5% w/w (SNI, 2010). Therefore, it cannot be used for human consumption or industrial purposes. The low level of NaCl in produced salt is due to the presence of impurities, like $MgSO_4$, $CaSO_4$, $MgCl_2$, KCl, and other soil impurities (Widjaja *et al.*, 2019). Impurities can be minimized using several purification methods.

There are a number of purification techniques that have been developed to increase the concentration of NaCl in salt, including the hydro extraction method (Astuti, Yulianti and Prasetya, 2016); (Nurhikmah Wahab, 2020), recrystallization with the addition of $Ca(OH)_2$, NaOH, and $CaCO_3$, precipitation and evaporation methods (Jumaeri *et al.*, 2021); (Tarmizi, Sunandar and Wibowo, 2021), purification using sodium hydroxide (NaOH) (Rahem and Kartika, 2020), ion exchange method (Pujiastuti, Sumada and Ngatilah, 2018), and iodization method using a spray mixer (Widjaja *et al.*, 2019). The presence of a binder can minimize these impurities. The binders used, according to (Jumaeri *et al.*, 2021), were NaOH, CaO, Ba(OH), and $(NH_4)_2CO_3$. Another usable binder to remove impurities in salt is alumina silicate materials, such as bentonite. Even though, bentonite is widely used for the removal of metal ions and other impurities from water (Musie and Gonfa, 2022), as well as the removal of both anionic and cationic pollutants (Wang *et al.*, 2014). The use of bentonite as a local salt purifier is never done before.

Metal ions and other impurities can be removed from water using bentonite (Musie and Gonfa, 2022). Anionic and cationic pollutants have both been removed using bentonite. Bentonite is a type of clay mineral with layered structures of the 2:1 type that includes mostly bentonite. Two silica (Si^{4+}) tetrahedral sheets and one alumina (Al^{3+}) octahedral sheet make up the fundamental structure of bentonite (Maged *et al.*, 2020). Bentonite is a class of clay minerals that mainly consists of montmorillonite. Because of its distinctive physicochemical properties, bentonite is an effective adsorbent for a variety of pollutants. These properties include low permeability, low cost, strong absorptive affinity with inorganic and organic substances, large specific surface, high porosity, and high cation exchange capacity (Liu *et al.*, 2018); (Uddin, 2017); (Ayub and Chaudhry, 2021); (Barakan and Aghazadeh, 2021); (Belousov *et al.*, 2019), good adsorption capacity, expansible interlayer space, flexible, and tunable acidity (Liu *et al.*, 2018), and micro and mesoporous particles.

Bentonite can swell when dissolved in water, so bentonite has non-permanent porosity and low thermal and hydrothermal stability. So, the activity produced by bentonite is not optimal. In other words, before bentonite can be used effectively in industry, some of its properties need to be enhanced through activation or treatment procedures. Bentonite is activated with inorganic acids (like H_2SO_4 or HCl) in order to replace the exchangeable ions of bentonite during chemical reactions (Rahimzadeh *et al.*, 2018). Strong acids and bases, including calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), zinc chloride ($ZnCl_2$), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), and sodium chloride, are used as activators (NaCl). Bentonites and other clays' mineralogical and physicochemical properties change significantly with acid and alkali treatments (Bayram *et al.*, 2021). In order to enhance the performance of metal impurities (Ca and Mg) in the recrystallization process and improve salt quality, the activation process can increase pore size and surface area.

For bentonite modification, the acid activation technique was used. Due to its high specific area, porosity, and adsorption capacity, activated bentonite in acid and alkaline was chosen for this investigation. The removal of calcium and magnesium from salt water to increase the content of NaCl was studied using modified bentonite. Bentonite structure characteristics were also investigated in both its natural and modified forms.

Materials and Methods

Materials

The materials used in this research were distilled water, aqua bidest, pH meter, Whatman 42 filter paper, and hydrochloric acid (HCl) were obtained from

E. Merck (Germany) in pro-analytical grade and used as it is without any further purification. Bentonite samples were collected from Aceh Tamiang Regency and salt samples from Aceh Timur Regency in Aceh Province.

Methods

Synthesis of HCl-Activated Bentonite

500 g of bentonite was crushed and repeatedly cleaned with distilled water for three hours. A centrifuge was used to filter the solution for 30 minutes at a speed of 500 rpm. The precipitate was then dried for six hours at 110 ^{o}C. The precipitate smoothed out and then sieved through a 270 mesh sieve. Additionally, bentonite was agitated for three hours while being activated with 0.1 M hydrochloric acid (HCl) (1:10). Following that, the mixture was filtered and dried at 170 °C for four hours.

Characterization Samples

On a Shimadzu Prestige-21 FT-IR spectrophotometer, the materials' Fourier Transforms Infra Red (FTIR) spectra (natural materials, activated bentonite, and activated zeolite) were captured. An X-Ray Diffraction (XRD) Shimadzu S-6000 was used to record the materials' X-ray diffractogram. The materials' surface morphology was evaluated using a scanning electron microscope (SEM) on a JEOL JSM-6510.

Salt Purification Method

Even before the crystallization process, the salt product is purified by HCl-activated bentonite as an impurity binder. The salt sample was first dissolved to create a saturated salt solution, and then a composite material made of HCl-activated bentonite was added in a ratio to the salt solution (1:10). Thus, it was agitated for three hours. The mixture was separated into solid and liquid components. The resulting filtrate was evaporated to crystallize. After being produced, the NaCl crystal product was dried in an oven for two hours at 110°C. The salt product was examined by NaCl concentration both before and after purification using an Atomic Absorption Spectrophotometer (AAS).

Results and Discussion

XRD Analysis

XRD analysis of acid activated bentonite aims to investigate diffraction patterns at a value of 2θ and the basal spacing of the crystalline lattice. The results of XRD analysis of the acid activated bentonite at $2\theta = 2\text{-}65^{o}$ are shown in Figure 1. The diffraction peak of natural bentonite at $2\theta = 19.7°$, 26.5°, 34.91°, 54.34°, and 61.80° by the standard pattern COD Card Number 96-901-0958 (Ruslan and Hardi, 2017), which identifies the bentonite structure as being of the montmorillonite type. The addition of hydrochloric acid (HCl) to bentonite did not change the basal spacing d_{001} on the diffractogram. The diffractograms of hydrochloric acid-activated bentonite in Figures 1(a) dan 1 (b) show the angular shift (2θ) and the distance between the planes becomes larger (shift to the right). This shift was caused by the reaction between bentonite and acid, which resulted in a decrease in the pore size of bentonite after activation by acid solution. This occurs due to the arrangement of layers on bentonite from a delamination structure (house to card) changes to a more regular arrangement (face to face) after the activation of hydrochloric acid which causes the pore size of the bentonite to be smaller after the activation process.

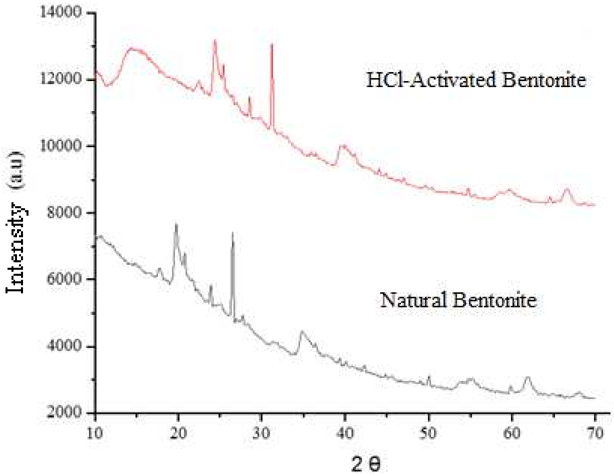
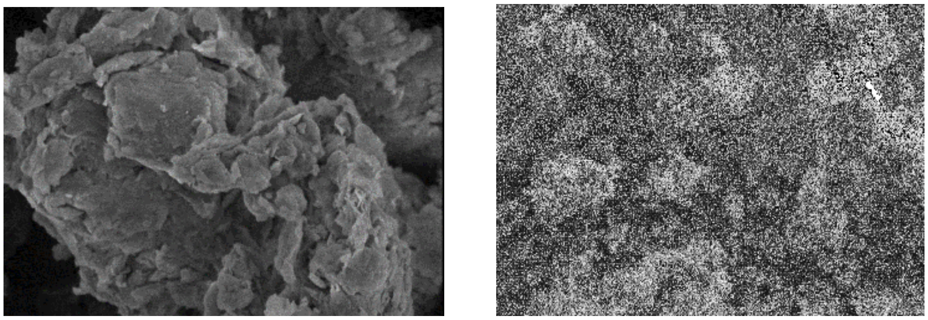


Figure 1. XRD Diffractogram (a) Natural Bentonite (b) HCl-Activated Bentonite

SEM Analysis

The results of morphological analysis of natural bentonite and acid activated bentonite using SEM with 500 times magnification can be seen in Figure 2.



(a) (b)

Figure 2. Micrograph of SEM (a) Natural Bentonite (b) HCl-Activated Bentonite

The surface of bentonite that has been activated with HCl forms large aggregates when compared to bentonite without activation. The surface of bentonite becomes more porous as a result of the leaching of cations and impurities after treatment with HCl. HCl activation in bentonite will result in more open pores and smaller sizes. Smaller pore size indicates a larger pore surface area, thereby increasing the adsorption capacity of heavy metals.

FTIR Analysis

Infrared spectra of bentonite and acid activated bentonite at a wave number between 4000- 400 cm^{-1} are presented in Figure 3. Figure 3 represented that the activation process of bentonite using HCl did not produce a significant change in the absorption of the characteristic wave number of the functional groups in bentonite, namely –OH derived from the bentonite framework and water molecules, Si-O-Si, and Al-Al-OH which is the structure in the octahedral sheet and tetrahedral in bentonite. Based on the FTIR spectrum in Figure 3, it can be seen that each spectra has almost the same absorption peak, there are only a few absorption peaks that experience a shift in wave number, namely wave number 365.46 cm^{-1} which is the OH stretching vibration of H_2O, shifting to 3693.84 cm^{-1} in acid activated bentonite. At wave number 1103.98 cm^{-1}, which is the asymmetric stretching vibration of Si-O-Si, it shifts to 1113.94 cm^{-1} in acid activated bentonite. This shows that bentonite has been activated (Lathifah, Yuliani and Wardhani, 2019). Al-Al-OH absorption decreased in wave number from 979.84 cm^{-1} to 920.08 cm^{-1} due to dehydroxylation and deallumination of bentonite (Ibigbami *et al.*, 2022). There is an absorption band at 1635.26 cm^{-1}, which represents the H-O-H bending vibration of water and an absorption band at 1036.98 cm^{-1} for the asymmetric stretching vibration of Si-O-Si (Ibigbami *et al.*, 20

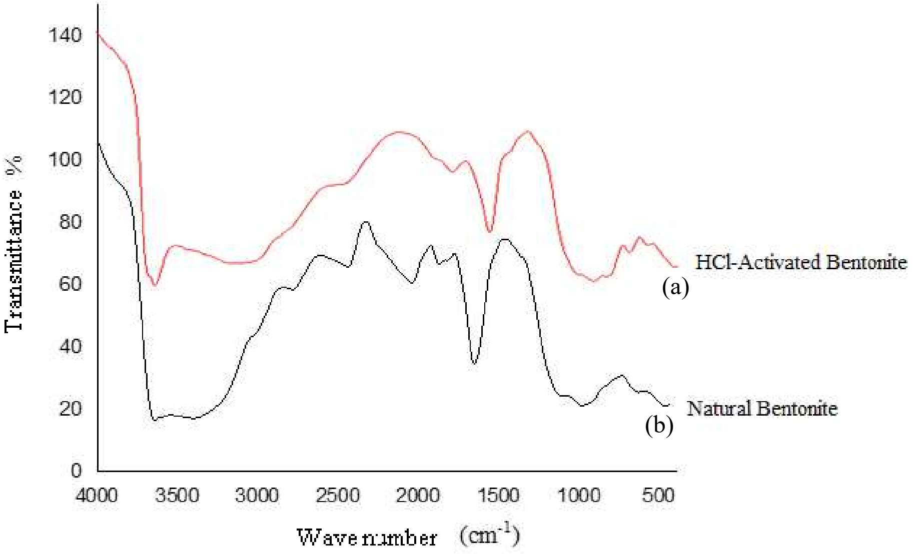


Figure 3. The spectrum of FTIR (a) Natural Bentonite (b) HCl-Activated Bentonite

The performance of bentonite can be increased through activation using strong acids including sulfuric acid (H_2SO_4), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and nitric acid (HNO_3). Acid activation can increase the number of protons (H^+) in the bentonite layer because acid activation can remove cations in the tetrahedral and octahedral layers, namely Si, Al, Fe, and Mg and dissolve impurities (Bijang and Sri, 2017). This will increase the surface area and pore diameter on the bentonite surface. The increase in acidity resulting from acid activation will form a larger pore size in bentonite (Bayram *et al.*, 2021).

Application Acid Activated Bentonite in Local Salt Purification

In this research, the activator used is a strong acid, namely HCl. The performance of acid-activated bentonite and natural bentonite as activators in the purification process of people's salt produced by salt farmers in East Aceh Regency was carried out by determining the levels of NaCl, Ca and Mg metals using Atomic Absorption Spectrophotometer (AAS). The levels of NaCl before and after recrystallization using a strong acid, namely HCl. NaCl content increased from 3032.5 mg/L to 3881.49 mg/L or an increase in the percentage of Na content of 27.99% after purification using HCl-activated bentonite. This happens because bentonite also has a lot of negative charges (O-) contained in the tetrahedral and octahedral layers bentonite contains a lot of negative charges that can bind impurities in salts such as Ca or Mg metals through electrostatic interactions. In addition, the activation process using HCl can increase the pore size, porosity, and surface area thereby increasing the adsorption ability of cationic metals such as Ca and Mg in the crystallization process and improve the quality of the recrystallization results. The decrease in metal content of Pb, Ca, and Mg after the recrystallization process using natural bentonite and acid activated bentonite is shown in Figure 5.

Figure 5 represented that HCl-activated bentonite can bind the impurities contained in the salt which causes the salt quality to decrease, namely Ca and Mg metals. The levels of Ca and Mg metals before and after the recrystallization process were 48.8899 mg/L to 51.3888 mg/L for Ca metal and 533.03 mg/L to 509.10 mg/L for Mg metal, respectively. The difference in the adsorption ability of bentonite to Ca and Mg metals is because Ca metal has a larger particle size than Mg metal so Ca metal will be more difficult to enter the pores of bentonite than Mg metal. This is evidenced by the decrease in metal content of Ca and Mg after the salt recrystallization process using HCl-activated bentonite and the increase in NaCl content as shown in Figure 4. Based on the results of the analysis, it can be concluded that the activation process using a strong acid such as HCl will improve the performance of bentonite in the adsorption of heavy metals contained in salt.

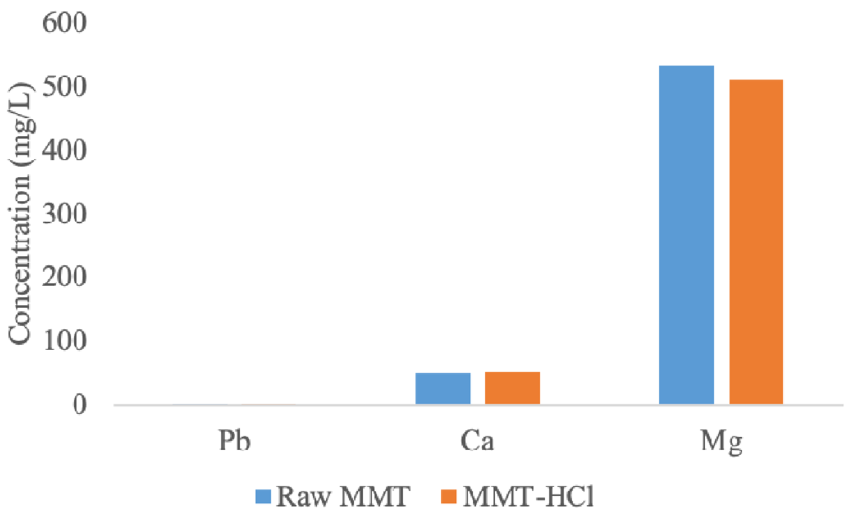


Figure 4. The results of AAS analysis of Pb, Ca, dan Mg (a) Natural Bentonite (b) Acid Activated Bentonite

Conclusion

Activation of bentonite using acid activation (HCl) has not led to changes to the physicochemical properties of bentonite. The basal spacing d_{001} on the diffractogram is unaffected by acid activation to bentonite, according to XRD analysis data, except for a slight shift toward a higher angle. According to the FTIR analysis, as the acid concentration rises, the stretching vibration of -OH shifts towards a lower wave number and the intensity decreases. Due to contact cations in the layer with the activator solution, the -OH of the octahedral becomes weak, reducing the wave number. However, the activation process using HCl can increase pore size and surface area, enhancing activated bentonite's ability to adsorb metal impurities like Mg during the crystallization process and improving the quality of the results of the recrystallization process. The activation process in bentonite resulted in an increase in NaCl levels from 3032.5 mg/L to 3881.49 mg/L accompanied by a decrease in Mg metal from 533.03 mg/L to 509.10 mg/L and increasing of Ca metal is 48.8899 mg/L to 51.3888 mg/L.

Acknowledgements

We thank Kemendikbud for funding this research through the grant of Penelitian Dasar Unggulan (PDU) Tahun 2022 with contract number 225/UN54/P/2022. We are also thankful to UPT. Basic Laboratory Universitas Samudra, MIPA Laboratory Syiah Kuala University, and Laboratory Politeknik Lhokseumawe for supporting facilities for synthesis and characterization in this research.

References

Astuti, R. P., Yulianti, C. H. and Prasetya, R. A. (2016). Pengaruh Lama Waktu Pengadukan Terhadap Pengikatan Impuritis untuk Meningkatkan Kadar NaCl Pada Garam Rakyat. *Journal of Pharmacy and Science*. 1(1). 9–14. https://doi: 10.53342/pharmasci.v1i1.46.

Ayub, N. and Chaudhry, M. N. (2021). Efficiency of Aluminium Pillared Bentonite Clays of Pakistani Origin (Peshawar and Samwal) on the Adsorption of Chromium Ions in Aqueous Solutions. *Polish Journal of Environmental Studies*. 30(2). 1039–1050. https://doi: 10.15244/pjoes/124739.

Barakan, S. and Aghazadeh, V. (2021). The Advantages of Clay Mineral Modification Methods for Enhancing Adsorption Efficiency in Wastewater Treatment: a Review. *Environmental Science and Pollution Research*. 28(3). 2572–2599. https://doi: 10.1007/s11356-020-10985-9.

Bayram, H. *et al.* (2021). Optimization of Bleaching Power by Sulfuric Acid Activation of Bentonite. *Clay Minerals*. 56(2). 148–155. https://doi: 10.1180/clm.2021.28.

Belousov, P. *et al.* (2019). Cesium Sorption and Desorption on Glauconite, Bentonite, Zeolite, and Diatomite. *Minerals*. 9(10). https://doi: 10.3390/min9100625.

Bijang, C.M. and Sri, D. (2017). Study of Bentonite Activation Using Sulphuric Acid and Its Application As an Adsorbent of Rhodamine B Dye. *Pattimura Proceeding Conf. Sci. Technol*. 1(1). 083-088. https://doi.org/10.30598/PattimuraSci.2017.ICBS3.083-088

Ibigbami, T. B. *et al.* (2022). Pristine and Activated Bentonite for Toxic Metal Removal from Wastewater. *Water Practice and Technology*. 17(3). 784–797. https://doi: 10.2166/wpt.2022.018.

Jumaeri *et al.* (2021). Recovery of High Purity Sodium Chloride from Seawater Bittern by Precipitation-Evaporation Method. *Journal of Physics: Conference Series*. 1918(3). https://doi: 10.1088/1742-6596/1918/3/032023.

Lathifah, T., Yuliani, N. and Wardhani, G. A. P. K. (2019). Bentonit Teraktivasi Asam Sulfat Sebagai Adsorben Dalam Pemurnian Pelumas Bekas. *Jurnal Sains Natural*. 9(1). 1. https://doi: 10.31938/jsn.v9i1.170.

Liu, J. *et al.* (2018). Highly Efficient Conversion of Glucose into Methyl Levulinate Catalyzed by Tin-Exchanged Bentonite. *Renewable Energy*. 120. 231–240. https://doi: 10.1016/j.renene.2017.12.104.

Musie, W. and Gonfa, G. (2022). Results in Engineering Adsorption of Sodium from Saline Water with Natural and Acid Activated Ethiopian Bentonite', *Results in Engineering*. 14(3). 100440. https://doi: 10.1016/j.rineng.2022.100440.

Nurhikmah Wahab, I. R. (2020). Analisa Pemurnian Garam Dengan Metode Hidro Ekstraksi Batch Dan Kontinue Di Kabupaten Jeneponto. *Jurnal*

Ilmiah Techno Enterpreneur Acta. 5(1). 10–11. Available at: file:///C:/Users/muhai/Downloads/189-61-318-1-10-20200801.pdf.

Pujiastuti, C., Sumada, K. and Ngatilah, Y. (2018). Application of Ion Exchange Method on Removal of The Ca^{2+}, Mg^{2+}, K^{+} and $SO4^{2-}$ Salt Solution. 1. 264–267. https://doi: 10.2991/icst-18.2018.55.

Rahem, M. and Kartika, A. G. D. (2020). Pengaruh Penambahan NaOH terhadap Peningkatan NaCl Garam Konsumsi. *Juvenil*. 1(4). 61–467. Available at: http://doi.org/10.21107/juvenil.v1i4.8935ABSTRAK.

Rahimzadeh, H. *et al.* (2018). Potential of Acid-Activated Bentonite and SO_3H-Functionalized MWCNTs for Biodiesel Production from Residual Olive Oil under Biorefinery Scheme. *Frontiers in Energy Research.* 6(12). 1–10. https://doi: 10.3389/fenrg.2018.00137.

Tarmizi, E., Sunandar, K. and Wibowo, A. D. K. (2021). Synthesis of Food Grade Salt From Brine Water of Tirta Sanita Bogor. *Jurnal Pangan dan Agroindustri*. 9(3). 65–172. https://doi: 10.21776/ub.jpa.2021.009.03.4.

Uddin, M. K. (2017). A Review on the Adsorption of Heavy Metals by Clay Minerals, with Special Focus on the Past Decade. *Chemical Engineering Journal*. 308. 438–462. https://doi: 10.1016/j.cej.2016.09.029.

Widjaja, T. *et al.* (2019). Iodization of Local Salt Based on Purification Technique using Saturated Brine Washing Method. *IOP Conference Series: Materials Science and Engineering*. 543(1). https://doi: 10.1088/1757-899X/543/1/012024.