DOI: 10.19184/ICL.v3i1.798

Synthesis and Characterisation of Bentonite/Poly(Acrylic Acid) Hybrid Material for Its Application as A Catalyst In Esterification of Glycerol With Acetic Acid

Hidayati N. M. Sholehah*[a], Tanti Haryati[a], Novita Andarini[a], Suwardiyanto[a], Yudi A. Sulistiyo[a]

Abstract: Bentonite/poly(acrylic acid) (BTAA) hybrid material commonly applied as superabsorbent was prepared via intercalation method coupled with in situ polymerisation of partially neutralised acrylic acid monomers. The structural characteristics of various BTAA ratios and their constituents were scrutinised using XRF, XRD, and FTIR. Basal spacing of BTAA hybrid materials decreased as a result of intercalation with polyacrylic acid. Interaction between bentonite and polyacrylic acid was also observed in the shifting and reduced intensity of O–H, C=O, and Si–O–Al absorption bands. Catalytic activity of BTAA was investigated through its ability to facilitate the esterification reaction of glycerol with acetic acid. The result suggests that catalytic activity is present in BTAA hybrid materials, as evidenced by the production of monoacetin and triacetin.

Keywords: Bentonite/poly(acrylic acid), catalytic activity, hybrid material, structural characteristics.

INTRODUCTION

Demands for hybrid materials technology in the past decade have been driving materials science and development at an increasing pace of improvement for well-established materials, as hybrid materials are acknowledged to demonstrate enhanced properties in contrast to their constituents [1]. Inorganic-organic hybrid such as bentonite/poly(acrylic acid) is one of the common hybrid materials synthesised from bentonite clay and polymerised acrylic acid monomers. Naturally occurring bentonite contains 70-85% montmorillonite [2], categorised as 2:1 phyllosilicate clay, known to have expanding properties due to its interlayer characteristics. The negatively charged interlayer space of montmorillonite hosts exchangeable cations such as Na^+, Ca^{2+}, Mg^{2+}, and K^+ as a result of isomorphous substitution in the tetrahedral or octahedral sheet [3, 4]. These unique characteristics render bentonite frequently used as filler [5], adsorbent, catalyst, and catalyst support [6]. However, its swelling capacity is limited to around 18 times its dry volume. Therefore, modification is necessary, especially with compounds known for their exceptionally high water absorption capacity [7]. Polyacrylic acid is a superabsorbent due to the occurrence of carboxyl groups at intervals of every two carbons along its chain, making this polymer a promising modifier [8, 9].

Modification of bentonite using polyacrylic acid can be performed via the intercalation method, which is arguably a cost-effective and straightforward process [10]. This method involves introducing an intercalant into the interlayer without altering the crystal structure of the clay. Intercalation of polyacrylic acid leads to the expansion of the interlayer distance in bentonite, consequently resulting in an increased basal spacing distance [11, 12]. Cukrowicz et al. [8] reported an increase in the basal spacing distance from 1.45 nm to 1.50 nm, whereas another study conducted by Wang et al. [13] attained only a negligible increase or even a decrease, as reported by You et al. [14]. The latter cases remain a challenge for the deployment of this method.

This study attempts to inspect the structural characteristics and swelling behaviour of bentonite/poly(acrylic acid) with various mass ratios of bentonite to acrylic acid monomers. The baseline ratio of 2:4 is adopted from the work of Zhumagaliyeva et al. [12] considering the material's structural rigidity, as the catalytic activity of the hybrid material is tested on the esterification of glycerol with acetic acid. The application of this material as a catalyst for the esterification of glycerol is relatively novel. Recent studies exploring the esterification of glycerol with acetic acid typically employ heterogeneous catalysts such as Amberlyst [15] and Lewatit [16] from the ion-exchange resins group, zeolites, and silica-alumina [17] from solid acids group. Nevertheless, the acidic properties inherent in this material underlie its potential as an acid catalyst crucial for converting glycerol into triacetin.

METHODS

Materials

Raw bentonite (BT) was obtained from Bondowoso, East Java, Indonesia. All the chemicals used in this study are of analytical grade and used without purification. Acrylic acid (AA, 99%) and MBA (99%) were purchased from Sigma-Aldrich, USA. HCl (37%), NaOH, KPS, glycerol (85%), and glacial acetic acid (100%) were supplied by Merck, Germany, whilst triacetin (97%) was purchased from LOBA Chemie, India.

Activation of Bentonite

Ca-bentonite was milled and then sieved through screens to obtain particle sizes ranging between 60-120 mesh. Further treatment of Ca-bentonite (20 g) with 5% of HCl solution (diluted from HCl 37%, 400 ml) at room temperature for 4 hours was conducted to yield H-bentonite (H-BT). The obtained H-BT was washed with distilled water and dried at 105°C for 2 hours [18].

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[a] HNM. Sholehah, Suwardiyanto, T. Haryati, N. Andarini, YA. Sulistiyo
Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Jember
*e-mail: hidayatinms@gmail.com

Synthesis of Bentonite/Poly(acrylic acid) (BTAA)

H-BT (3, 6, and 9 g) was dispersed in 20 mL distilled water for 2 hours at room temperature to form a suspension [12]. Partially neutralised AA (12 g) was prepared by dripping it into NaOH (5 M, 26.6 mL) solution under an ice bath condition with vigorous stirring. The H-BT suspension was placed in a three-neck flask, and then the partially neutralised AA was introduced into the suspension, followed by refluxing at 60°C for 1 hour. KPS (0.1 mol.%) was added first and stirred for 5 minutes before adding MBA (0.5 mol.%). The mixture was refluxed by increasing the temperature to 80°C until gel formed [12, 14, 19]. The resulting bentonite/poly(acrylic acid) (BTAA) gels with 1:4, 2:4, and 3:4 ratios were dried at 100°C and then milled into powder [14].

Characterisation

The chemical composition of BT and H-BT was revealed using XRF (Thermo Scientific Niton XL3t GOLDD+). Powder X-ray diffraction (XRD) was employed to investigate the basal spacing distance of BT, H-BT, and BTAA. The characterisation was operated on a Phillips X-Pert PRO PANalytical diffractometer with Cu Kα radiation (λ = 0.15406 nm) and scanned at 2θ = 5-60°. Functional groups of the materials were observed by means of FTIR spectroscopy (Thermo Scientific Nicolet Is10) at 400-4000 cm-1.

Determination of Swelling Degree

BTAA (1 g) was immersed in 200 mL of distilled water at room temperature and allowed to swell for 1, 3, 6, 8, 9, and 10 hours [12]. Separation of swollen BTAA from the unabsorbed water was performed by vacuum filtration, followed by weighing. The swelling degree (Q) was calculated using the equation 1. The mass of the dry BTAA is denoted as W1, while W2 represents the mass of the swollen BTAA.

$$Q = \frac{W_2 - W_1}{W_1} \tag{1}$$

Catalytic Activity Test for Esterification of Glycerol

Glycerol and acetic acid with a 1:5 molar ratio were heated to 100°C separately. Acetic acid was then transferred into a three-neck flask containing glycerol and equipped with a reflux set, followed by the loading of BTAA 1:4 catalyst (10 wt.% w.r.t the mass of glycerol) [17], which was treated with HCl (1 M) and stirring prior to use [16]. The reaction was carried out at 100°C for 8 hours [17]. The sample analysis was recorded on a Thermo Scientific Trace 1310 gas chromatograph equipped with a TR-Wax column (length = 30 m, ID = 0.25 mm, df = 0.25 μm) and FID detector.

RESULT AND DISCUSSION

Structural Characteristics of Activated Bentonite

The structural studies of raw bentonite (BT) and activated bentonite (H-BT) were conducted using XRF and XRD. The chemical composition of raw bentonite revealed using XRF analysis is as follows: Ca 11.71%, Si 17.88%, Al 3.44%, Mg 0.65%, and Fe 3.07%, confirming that bentonite used in this study is Ca-bentonite. This composition changes following acid activation to Ca 0.81%, Si 23.39%, Al 3.98%, Mg 0.20%, and Fe 3.49%. During an acid activation process, acid attack occurs on the surface and layer of the clay, causing the substitution of exchangeable cations, and sometimes leads to the dissolution of structural cations due to the partially dissolved Al_2O_3 and Fe_2O_3 [20]. The results show that calcium content decreases significantly, indicative of cation exchange between Ca^{2+} in the interlayer and H^+ carried by the acid. The main structure of montmorillonite is relatively not altered during the acid activation proven by increasing contents of Si, Al, and Fe [21]. In contrast, Mg content decreases due to leaching from the interlayer and octahedral sheet.

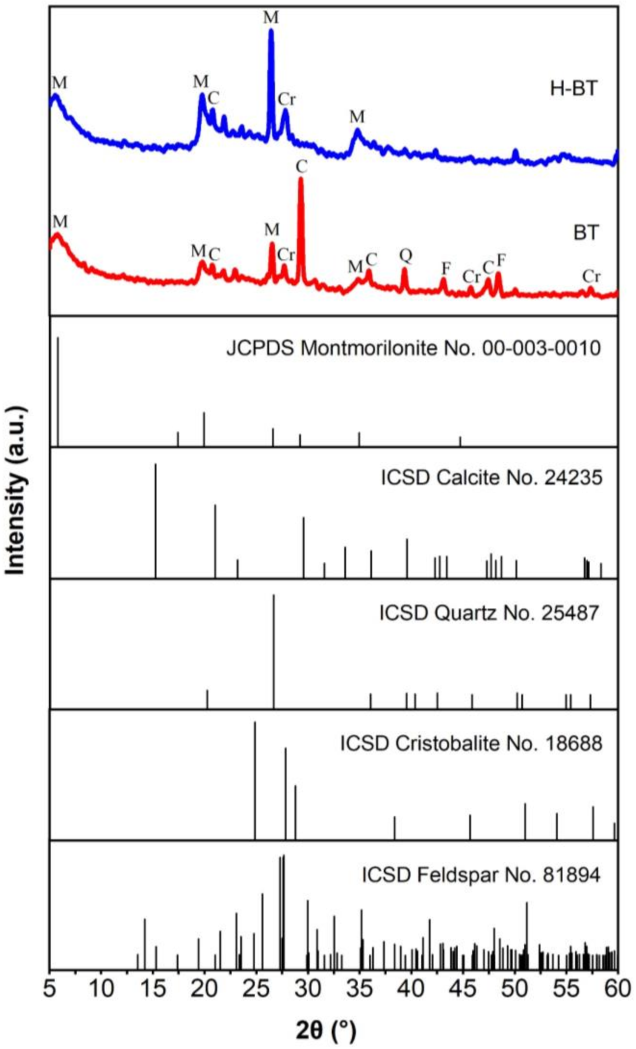

Figure 1. Diffractogram of raw bentonite (BT) and H-bentonite (H-BT)

X-ray diffraction studies of BT and H-BT show noticeable differences in their diffraction patterns (Figure 1). Diffraction pattern of BT reveals montmorillonite peaks as the principal constituent of the clay at 2θ = 5.774°, 19.709°, 26.516°, and 34.907° based on JCPDS database No. 00-003-0010. Other compounds seen as impurities are also present in the sample, namely calcite at 2θ = 20.752°, 29.346°, 35.922°, and 47.452° (ICSD No. 24235), quartz at 2θ = 39.297° (ICSD No. 25487), cristobalite at 2θ = 27.698°, 45.763°, and 57.346° (ICSD No. 18688), and feldspar at 2θ = 43.134° and 48.384° (ICSD No. 81894). Following the acid activation, a change in position happens to montmorillonite d_{001} peak at 2θ = 5.774° in BT to 5.634° in H-BT. This shifting is directly associated with increased basal spacing distance from 1.529 nm to 1.567 nm. The crystallinity of montmorillonite is not reduced by acid activation, as observed in the increased peak intensity. Most peaks corresponding to the impurities almost disappear entirely from the diffraction pattern of H-BT, retaining only a single calcite and cristobalite peak. The elimination of calcite due to acid attack corroborates the decrease in calcium content [21], as previously shown by the XRF analysis.

Structural Characteristics of BTAA Hybrid Materials

The effect of bentonite modification using polyacrylic acid is depicted in Figure 2. In general, modification causes shifting in the d_{001} peak to 2θ = 7.825°, 7.798°, and 7.777°, thus leading to a decrease in the basal spacing distances to 1.129 nm, 1.133 nm, and 1.136 nm, respectively, for BTAA 1:4, 2:4, and 3:4 ratio. Hydrogen bond formation due to the presence of –OH group on the surface of bentonite and –COOH group of polyacrylic acid may give rise to the decrease in basal spacing [12, 13]. Despite the reduction in basal spacing distances of the hybrid materials, an observable trend indicates an increase in basal spacing related to higher bentonite concentrations. Changes in the bentonite chemical environment after intercalation with polyacrylic acid also generate an emergence of unresolved peaks at 2θ = ~30-31°, speculated to be polyacrylic acid peaks.

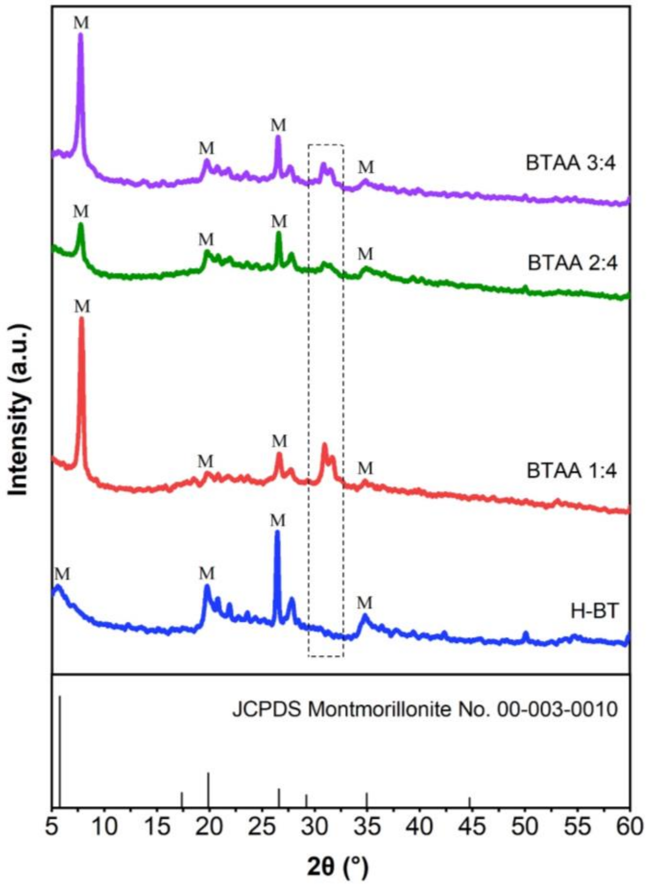

Figure 2. Diffractogram of H-bentonite (H-BT) and bentonite/poly(acrylic acid) (BTAA)

Structural characteristics of the hybrid materials are also studied by interpreting IR spectra along the regions of ~3000-3600 cm^{-1} and ~1000-1700 cm^{-1}, as shown in Figure 3. IR spectra of BTAA exhibit a broad absorption band at ~3360-3370 cm^{-1} assigned to the O–H stretching vibration. The band intensity is relatively lower and accompanied by a shift in its position compared to H-BT (~3683 cm^{-1}) and PAA (~3333 cm^{-1}). A weak absorption band due to carboxylic acid C=O stretching vibration appears in the ~1700 cm^{-1} region, undergoing a shift towards higher wavenumber in contrast to C=O vibration in PAA (~1680 cm^{-1}). N–H bending vibration due to amide functional group of MBA emerges at ~1540-1560 cm^{-1} with no observable reduction in intensity. Unsaturated C=C vibration is no longer detected for the hybrid materials, suggesting a complete polymerisation has occurred. The absorption band of Si–O–Al, characteristics of bentonite, shifts to higher wavenumber at ~1067 cm^{-1}.

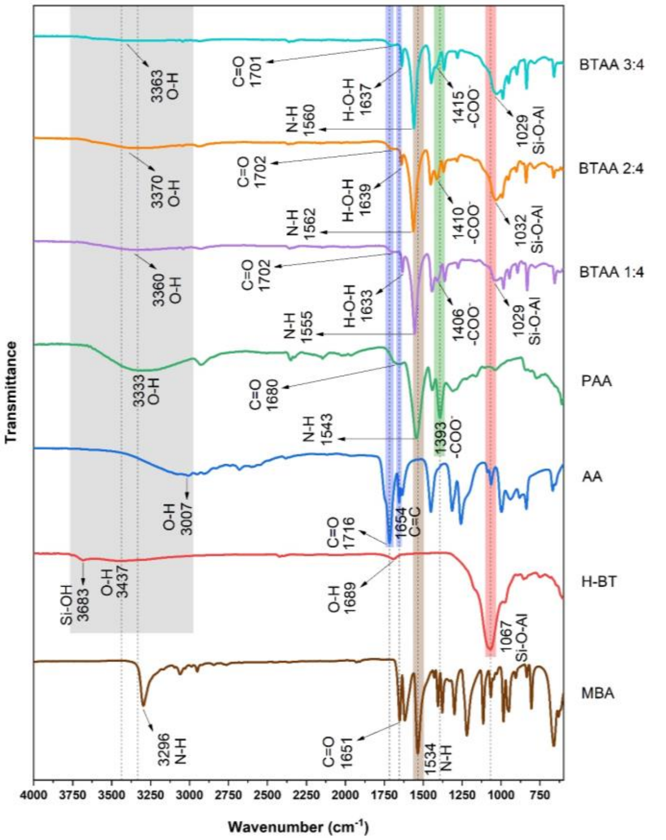

Figure 3. IR spectra of MBA, H-Bentonite (H-BT), acrylic acid (AA), polyacrylic acid (PAA), and BTAA hybrid materials

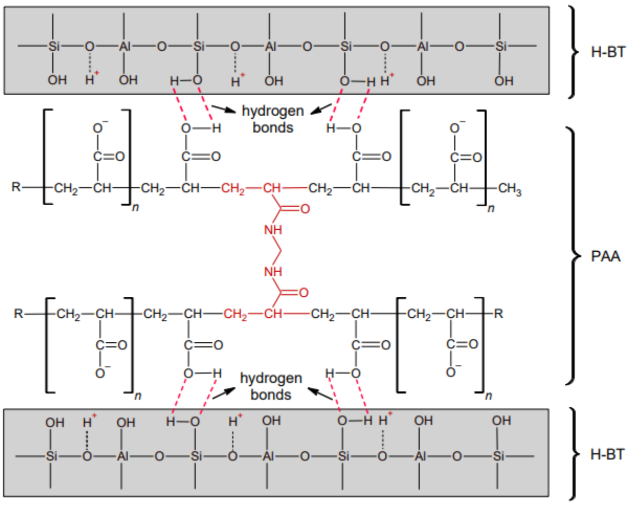

Figure 4. Proposed structure and interaction of BTAA

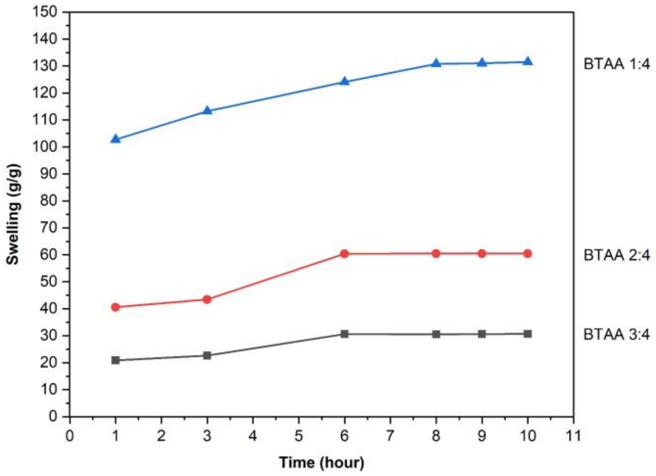

Figure 5. Swelling degree of BTAA hybrid materials

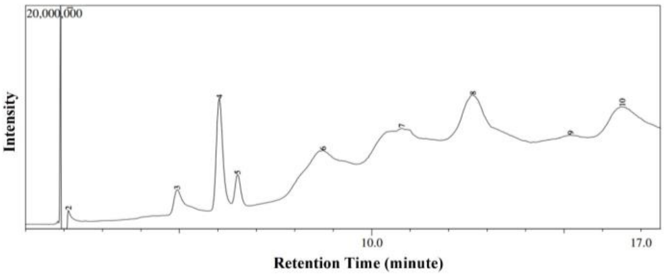

Figure 6. GC-MS results of esterification product catalysed by BTAA 1:4

The observed shifts in O–H, C=O, and Si–O–Al absorption bands indicate the potential interaction between bentonite and polyacrylic acid. This data also confirms the formation of hydrogen bonds between the –OH groups in the H-BT framework and the –COOH groups carried by polyacrylic acid as the predominant interaction [13], as illustrated in Figure 4. This interaction is further supported by the trend showing higher bentonite concentrations lead to a decrease in the intensity of the O–H and C=O absorption peaks due to the increased probability of interactions altering the surrounding chemical environment. Based on the FTIR and XRD analysis, it is evident that polyacrylic acid has been successfully intercalated into the interlayer of bentonite.

The swelling behaviour of the resulting hybrid materials is also investigated as a physical property of the hybrid materials. Figure 5 depicts that BTAA with a 1:4 ratio reaches the maximum swelling degree of 130 g/g after 8-9 hours of coming into contact with water. In comparison, BTAA with 2:4 and 3:4 ratios only perform at a maximum of 60 g/g and 30 g/g, respectively. The trend shows the swelling capacity of BTAA is directly affected by bentonite concentration of which increasing it can cause a decrease in the swelling capacity. It appears that the presence of bentonite in the polymer matrix results in a limitation of –COOH groups available for interaction with water molecules arising from hydrogen bonds formation between the PAA carboxylic groups and hydroxyl groups on the surface of bentonite [13, 14]. This leads to the formation of a more compact material structure. The data showing an inverse relationship between the increased basal spacing and the swelling capacity of BTAA provides indicative evidence that swelling is confined to the polyacrylic acid located external to the interlayer of bentonite.

Catalytic Activity of BTAA Hybrid Materials

Table 1. List of compounds present in esterification product catalysed by BTAA 1:4

Peak Number	Compound Name
1	Acetic acid
2	2-Undecanol
3 and 4	Monoacetin
5	Triacetin
6, 8, and 10	1-Pentacontanol
7	1,3-Dioxolan
9	Cyclohexane

The catalytic activity of the hybrid materials is assessed through gas chromatography (GC). The results show comparable activities across different mass ratios. Gas chromatography-mass spectrometry (GC-MS) is additionally utilized to elucidate the compounds present in the esterification product, as detailed in Table 1 and illustrated in Figure 6. The GC-MS analysis reveals that the catalyst facilitates the conversion of glycerol to monoacetin and triacetin with an abundance of 24.05% and 4.85%, respectively. The emergence of two monoacetin peaks suggests that both monoacetin isomers formed during the reaction. GC-MS results also indicate the presence of acetic acid (5.38%) in the sample, as it has not undergone a complete conversion. Meanwhile, the glycerol peak is not detected, indicating that glycerol has been fully converted. The GC-MS analysis results also suggest that the BTAA catalyst yields additional byproducts alongside water formation, likely caused by dissolved homopolymers in both glycerol and acetic acid during the esterification reaction. It can be inferred that the BTAA hybrid material exhibits low catalytic activity. The acid catalyst employed in this esterification reaction must possess sufficient strength to effectively facilitate the reaction. The results suggest that the hybrid material does not meet the necessary criteria for catalytic strength, in relation to the acidity of polyacrylic acid. Furthermore, the potential formation of hydrogen bonds between polyacrylic acid and the surface of bentonite may limit the availability of –COOH groups for interaction, contributing to the observed low acidity of polyacrylic acid. This interaction is a significant factor that may account for the inadequate catalytic performance of polyacrylic acid.

CONCLUSION

Intercalation of polyacrylic acid into the interlayer spaces of bentonite changes the chemical environment of both materials. The structural analysis reveals hydrogen bond formation as the primary interaction occurring in the framework of the resulting BTAA hybrid material. The degree of swelling is likely governed by increasing bentonite concentration, leading to decreased swelling capacity of BTAA. The hybrid material also exhibits low catalytic activity for the esterification of glycerol with acetic acid, yielding 24.05% monoacetin and 4.85% triacetin.

REFERENCES

[1] S. H. Mir, L. A. Nagahara, T. Thundat, P. Mokarian-Tabari, H. Furukawa, and A. Khosla, "Review-Organic-Inorganic hybrid functional materials: an integrated platform for applied technologies," *J. Electrochem. Soc.*, vol. 165, no. 8, pp. B3137-B3156, 2018.

[2] P. I. Au, P. Pillai, and Y. K. Leong, "Ageing and collapse of Bentonite gels - Effects of Mg(II), Ca(II) and Ba(II) ions," *Appl. Clay Sci.*, vol. 114, pp. 141-150, 2015.

[3] X. Li, Q. Li, S. Yang, and G. Yang, "Swelling of clay minerals: Dual characteristics of K+ ions and exploration for critical influence factor," *Phys. Chem. Chem. Phys.*, vol. 21, no. 4, pp. 1963-1971, 2019.

[4] N. Yener, C. Biçer, A. D. Pekdemir, Y. Sarıkaya, and M. Önal, "Preparation and characterization of nanoporous powders from bentonite by hydrochloric acid leaching and using as bleaching earth," *SN Appl. Sci.*, vol. 2, no. 4, 2020.

[5] O. V. Alekseeva, A. N. Rodionova, N. A. Bagrovskaya, A. V. Agafonov, and A. V. Noskov, "Effect of the bentonite filler on structure and properties of composites based on hydroxyethyl cellulose," *Arab. J. Chem.*, vol. 12, no. 3, pp. 398-404, 2019.

[6] F. Bergaya and G. Lagaly, "Developments in clay science 5: Handbook of clay science." Elsevier Ltd, Amsterdam, 2013.

[7] J. Dehn and S. R. McNutt, *Volcanic Materials in Commerce and Industry*, Second Edi. Elsevier Inc., 2015.

[8] S. Cukrowicz *et al.*, "Organobentonites modified with poly(Acrylic acid) and its sodium salt for foundry applications," *Materials (Basel).*, vol. 14, no. 8, pp. 1-18, 2021.

[9] L. Chang, L. Xu, Y. Liu, and D. Qiu, "Superabsorbent polymers used for agricultural water retention," *Polym. Test.*, vol. 94, p. 107021, 2021.

[10] M. Rajapakse *et al.*, "Intercalation as a versatile tool for fabrication, property tuning, and phase transitions in 2D materials," *2D Mater. Appl.*, vol. 5, no. 1, 2021.

[11] A. J. Jacobson and L. F. Nazar, Intercalation Chemistry. 2011.

[12] S. N. Zhumagaliyeva, R. S. Iminova, G. Z. Kairalapova, M. M. Beysebekov, M. K. Beysebekov, and Z. A. Abilov, "Composite polymer-clay hydrogels based on bentonite clay and acrylates: Synthesis, characterization and swelling capacity," *Eurasian Chem. J.*, vol. 19, no. 3, pp. 279-288, 2017.

[13] X. Wang, Y. Zheng, C. Zhang, and L. Zong, "Preparation and swelling properties of hydrolysis-resistant superabsorbent composite based on acrylic acid and sodium bentonite," *Int. J. Polym. Anal. Charact.*, vol. 25, no. 5, pp. 300-314, 2020.

[14] X. You, J. Cao, X. Liu, J. Lu, and X. Chen, "Synthesis of the poly(acrylic acid-acrylic sodium) bentonite composite and its adsorption of Cd(II)," *Asia-Pacific J. Chem. Eng.*, vol. 12, no. 1, pp. 65-74, 2016.

[15] K. V. Caballero, H. Guerrero-Amaya, and V. G. Baldovino-Medrano, "Revisiting glycerol esterification with acetic acid over Amberlyst-35 via statistically designed experiments: Overcoming transport limitations," *Chem. Eng. Sci.*, vol. 207, pp. 91-104, 2019.

[16] L. Setyaningsih, F. Siddiq, and A. Pramezy, "Esterification of glycerol with acetic acid over Lewatit catalyst," *MATEC Web Conf.*, vol. 154, pp. 2–5, 2018.

[17] T. V. . Kotbagi, S. L. Pandhare, M. K. Dongare, and S. B. Umbarkar, "In situ formed supported silicomolybdic heteropolyanions: Efficient solid catalyst for acetylation of glycerol," *J. Environ. Anal. Chem.*, vol. 02, no. 05, pp. 1-6, 2015.

[18] N. Indraswati, Struktur Bentonit Terinterkalasi Fe_3O_4, University of Jember, 2022.

[19] M. Stirner, "Clay linked Gels Mechanical Enhancement of Hydrogels by Incorporation of Clay Minerals," University of Bayreuth, 2014.

[20] F. Bergaya, B. K. G. Theng, and G. Lagaly, Handbook of Clay Science, vol. 1, no. 2. 2006.

[21] T. Taher, D. Rohendi, R. Mohadi, and A. Lesbani, "Thermal and Acid Activation (TAA) of bentonite as adsorbent for removal of methylene blue : A kinetics and thermodynamic study," *Chiang Mai J. Sci.*, vol. 45, no. 4, pp. 1770-1781, 2018.