

Preparation of Environmentally Friendly Adsorbent Using Oil Palm Boiler Ash, Bentonite and Titanium Dioxide Nanocomposite Materials

Nurdin Bukit¹, Eva Marlina Ginting¹, Erna Frida^{2*}, Bunga Fisikanta Bukit³

¹ Department of Physics, Universitas Negeri Medan, Jl. Willièm Iskandar Pasar V Medan Estate, 2022, Medan, Indonesia

² Department of Physics, Universitas Sumatera Utara, Jl. Dr. T. Mansur No. 9 Padang Bulan, Kec. Medan Baru, 20155, Medan, Indonesia

³ Department of Physics, Universitas Quality Berastagi, Desa Lau Gumba, 22153, Berastagi, Indonesia

* Corresponding author's e-mail: ernafridatarigan@usu.ac.id

ABSTRACT

Using the products derived from agricultural wastes as low-cost adsorbent materials to remove organic or inorganic contaminants would be ideal, as these materials are readily available in many countries. This study aimed to prepare environmentally friendly adsorbents made from nanocomposite OPBA / Bentonite / TiO₂. The coprecipitation method was used in preparing OPBA, and CTAB surfactant was added in bentonite preparation. Meanwhile, the manufacture of TiO₂ was carried out using the sol-gel method. Characterization was done by XRD, FTIR, SEM, and BET. The adsorbent spectra did not show a significant shift in absorption where the O-H bonds were becoming weaker due to the presence of TiO₂ in the interlayer of bentonite. Another possibility is due to the influence of calcination and heating. The O-H groups of H₂O are hydroxylated and dehydrated from within between layers. The formation of the composite OPBA/TiO₂/Bentonite does not change the crystallinity of TiO₂ significantly. This proves that there is no decrease in photocatalyst activity after the addition of OPBA and bentonite. The morphology of the whole sample has a flake-like structure that has pores. The addition of OPBA into Bentonite/TiO₂ causes a decrease in the specific surface area of the sample.

Keywords: adsorbent, nanocomposite, bentonite, TiO₂, Boiler Ash.

INTRODUCTION

Heavy metal pollution in the environment is a severe problem. Heavy metals directly impact human life, as they accumulate in the food chain, even in low amounts. Some heavy metals were found to have polluted water and exceeded the limit dangerous to life. A nano-adsorbent is required to remediate heavy metals (Lubis et al., 2022). The adsorption technique is an effective water filtration technique, because it effectively removes various contaminants and heavy metals, making its use easy (Wang et al., 2010). Using by-products derived from agricultural wastes as low-cost adsorbent materials to remove organic or inorganic contaminants would be ideal, as these materials are readily available

in many countries. Oil Palm Boiler Ash (OPBA) is biomass with silica (SiO₂) content that has the potential to be utilized (N. Bukit et al., 2019; Frida, Bukit, et al., 2022). Palm ash from the combustion of palm kernel shells and fruit fibers contains the chemical element Silica, 48.5% (B.F. Bukit, Frida, Humaidi, & Sinuhaji, 2022b; B.F. Bukit, Frida, Humaidi, Sinuhaji, et al., 2022; Ginting, Bukit, Frida, et al., 2020). It is reported that 4 million tonnes of OPBA are produced annually, which is expected to increase due to the increasing global demand for palm oil (Abdul Khalil et al., 2011). Research shows that OPBA can be used as an effective adsorbent for Cr(III) (Chun et al., 2001)

Several studies on OPBA as adsorbents include. Modifying raw OPBA into OPBA

composite can increase the surface area of the adsorbent. The larger the surface area of the adsorbent, the greater the adsorption area is. OPBA composites have excellent potential to remove COD, ammonia nitrogen, nitrate, and phosphorus from wastewater. Its fast absorption and high adsorption capacity, coupled with its natural abundance in the environment, is a low-cost adsorbent that can be used in various wastewater treatment applications (Ginting, Bukit, Motlan, et al., 2020; Manikam, Halim, & Hanafiah, 2019; Manikam, Halim, Hanafiah, et al., 2019).

Natural agro minerals, such as bentonite have unique catalytic and adsorption properties. Bentonite is one of the most promising types of materials as a safe nanotechnology material (N. Bukit et al., 2018; Sirait et al., 2017, 2018; Toor et al., 2015). The adsorption ability of natural bentonite is not realized to its full potential when no modification is made. Therefore, bentonite modification is required (Ginting et al., 2017). The ability of bentonite can be increased by the pillarization process and the calcination process. The intercalation of polycation and calcination produces a bentonite layer that is stable and constant at high temperatures. The polycation that can be used is Titanium Dioxide (TiO_2). TiO_2 has a large specific surface area that allows it to be combined with other materials without blocking the pores of these materials. Bentonite pillarization using Ti cations is expected to increase the basal distance and specific surface area (Basuki et al., 2019; Zuo et al., 2015). The adsorbent composite materials that have been studied include bentonite- TiO_2 , bentonite-iron oxide, OPBA-zeolite/chitosan, TiO_2 -natural zeolite, biosilica/chitosan (Fatimah, 2012; Khanday et al., 2017; Liu et al., 2015; Sutrisno et al., 2016). In this study, the preparation of environmentally friendly adsorbents made from nanocomposite OPBA, Bentonite, and TiO_2 was carried out to adsorb heavy metals.

MATERIAL AND METHOD

Material

The material used in the study include OPBA from PT. DPI (Dhajaja Putra Indonesia) Asahan District North Sumatra Indonesia, Bentonite, TiCl_4 , 6M HCL, NH_4OH Merck Pro Analis.

Preparation of OPBA and bentonite nanoparticle

OPBA waste was dried and calcined at 500°C for 5 hours and then milled with a ball mill type Planetary Ball Mill for 10 hours with a rotation of 250 rpm filtered using a 200 mesh sieve. Then, it was mixed OPBA with 7 M HCl at 70°C for 4 hours. OPBA was mixed with NH_4OH at 70°C for 4 hours and then neutralizing the pH (B. F. Bukit, Frida, Humaidi, Sinuhaji, et al., 2022). Meanwhile, bentonite was calcined for 5 hours at 700°C . Bentonite was milled with a ball mill for 10 hours with a rotation of 250 rpm. Then, 0.2 moles of CTAB were mixed with distilled water. Bentonite, CTAB, and distilled water were mixed at a temperature of 100°C for 4 hours (Frida, Rahmat, et al., 2022).

Preparation of TiO_2 nanoparticle

TiCl_4 was mixed with NH_4OH at a temperature of 70°C and a stirring speed of ± 300 rpm. Then, 0.5 M solution $(\text{NH}_4)_2\text{SO}_4$ was added. The result of the reaction was in the form of a gel, separated and washed with deionized water to remove chlorine ions. Then, the gel was dispersed into an ethanol solution to remove water and reduce agglomeration during the drying process. The resulting TiO_2 was then dried at 60°C for 48 hours.

Preparation of OPBA, Bentonite, and TiO_2 nanocomposite

The preparation of OPBA, Bentonite, and TiO_2 nanocomposite was done by mixing them with NaOH and stirring them for 5 hours using a stirrer, then washed with deionized water. Furthermore, it was placed in the furnace at a temperature of 500°C for 3 hours.

RESULTS AND DISCUSSION

FTIR analysis of adsorbent

FTIR analysis was carried out to determine the changes in functional groups that occurred in the compound. The changes in functional groups experienced by the compound indicate a chemical interaction between Natural rubber and filler. This infrared spectrum is analyzed by observing the typical frequencies of the functional group of

the sample FTIR spectra. The FTIR used is the Agilent Cary 630 FTIR. This flexible benchtop FTIR instrument offers high performance and exceptional ease of use in an ultra-compact design. The FTIR of the adsorbent is shown in Figure 1.

Broadband around 629 cm^{-1} may be due to vibration of Ti-O bonds on the titanium dioxide lattice. However, involvement of TiO_2 particles in the absorption is difficult to evaluate in the low spectrum region as well, because this band overlaps with the vibrations of the clay skeleton (B. F. Bukit, Frida, Humaidi, & Sinuhaji, 2022a; Đukić et al., 2015). Vibration from hydroxyl groups was observed at peak widths of about $3100\text{ to }3600\text{ cm}^{-1}$. The typical infrared absorption band of montmorillonite is observed in bentonite. The bands are Al (Mg) OH strain 3614 cm^{-1} , intermolecular hydrogen bonding H-O-H strain 3417 cm^{-1} , and Si-O-Si. The absorption band shows

the deformation of OH group and strain vibration, indicating the presence of weak molecules in TiO_2 (N. Bukit et al., 2021). This property is needed in photocatalysis because the OH group can react with holes and prevent the recombination of electron-hole pairs. The absorption band $2884\text{--}2886\text{ cm}^{-1}$ is the C-H vibration of the methyl and methylene groups of the CTAB surfactant residue (Zhuang et al., 2017). The wave number $3000\text{--}3600\text{ cm}^{-1}$ is the O-H stretching vibration of H_2O trapped in the interlayer of bentonite. The adsorbent spectra did not show a significant shift in absorption where the O-H bonds were becoming weaker due to the presence of TiO_2 in the interlayer of bentonite. Another possibility is due to the influence of calcination and heating. The O-H groups of H_2O are hydroxylated and dehydrated between layers.

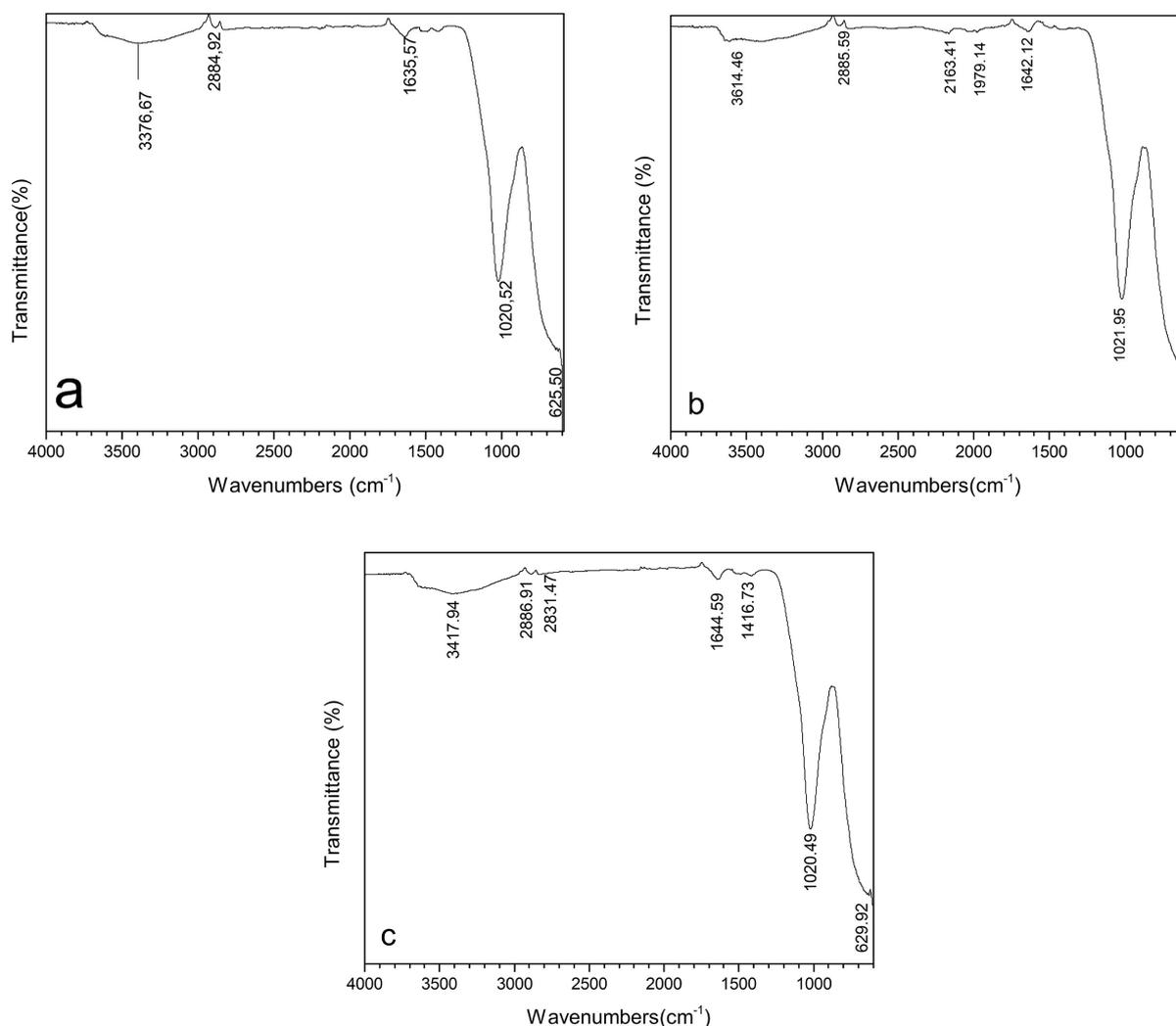


Fig. 1. FTIR Adsorbent: a. OPBA/Bentonite/ TiO_2 (0:25:25 g), b. OPBA/Bentonite/ TiO_2 (10:25:25 g), c. OPBA/Bentonite/ TiO_2 (15:25:25 g)

XRD analysis of adsorbent

XRD characterization is useful for obtaining diffraction patterns and crystal structures. The XRD used is the Shimadzu 6100 type (40 kV, 30 mA) with a wavelength of $\text{Cu-K}\alpha_1 = 1.5405 = 0.15406 \text{ nm}$, with a rate of $2^\circ/\text{min}$ at an angle range of $2\theta = 5\text{--}70^\circ$. The XRD of the adsorbent is shown in Fig 2.

Measurement of diffraction with an x-ray diffractometer produces data in the form of a diffraction pattern consisting of measurement data for 2θ angles and peak intensity at related angles. Using the Match-Phase Identification from Powder Diffraction Data application and the COD (Crystallography Open Database) database, the compounds that match the peaks at an angle of 2θ can be identified, given the results of the analysis. Table 1 shows the results of the XRD adsorbent data.

Reflection on 2θ indicates the crystal phase contained in the OPBA/ TiO_2 /Bentonite composite is anatase crystal phase. The result shows that the formation of the composite OPBA/ TiO_2 /Bentonite does not change the crystallinity of TiO_2 significantly. This proves that there is no decrease in photocatalyst activity after the addition of OPBA and bentonite.

SEM analysis of adsorbent

Scanning Electron Microscope can provide the information about the surface topography of a specimen. SEM characterization was carried out using the SEM TM3030 model. The morphology of the nanocomposite is shown in Figure 3.

The whole sample has a flake-like structure that has pores. PH plays an essential role in the formation of the previously synthesized TiO_2 . On the basis of several studies, variations in surface charge depend on the pH used in the synthesis process. In addition, agglomeration occurs on some parts of the surface. The agglomeration that occurs makes the surface morphology found homogeneous in certain areas (Ibrahim & Sreekantan, 2011).

BET analysis of adsorbent

The surface area analysis used is the analysis with the Brunauer, Emmet and Teller (BET) method, conducted using Quantachrome Nova 4200e. Figure 4. Shows BET of Adsorbent. Desorption is the removal of gas molecules from available solid surfaces, including surfaces inside open pores. Adsorption is the attachment of gas molecules to available solid surfaces, including surfaces in open pores.

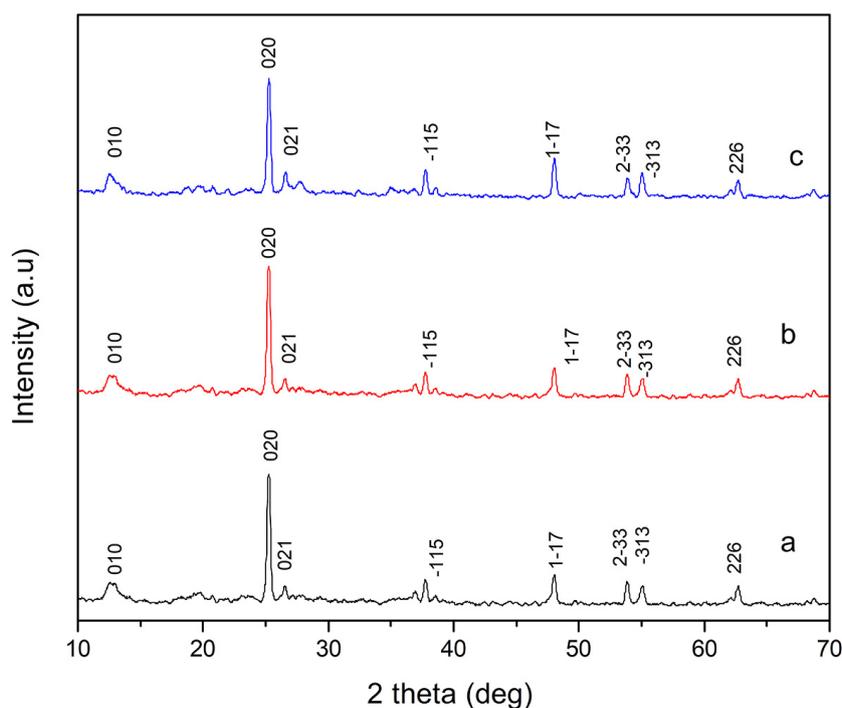
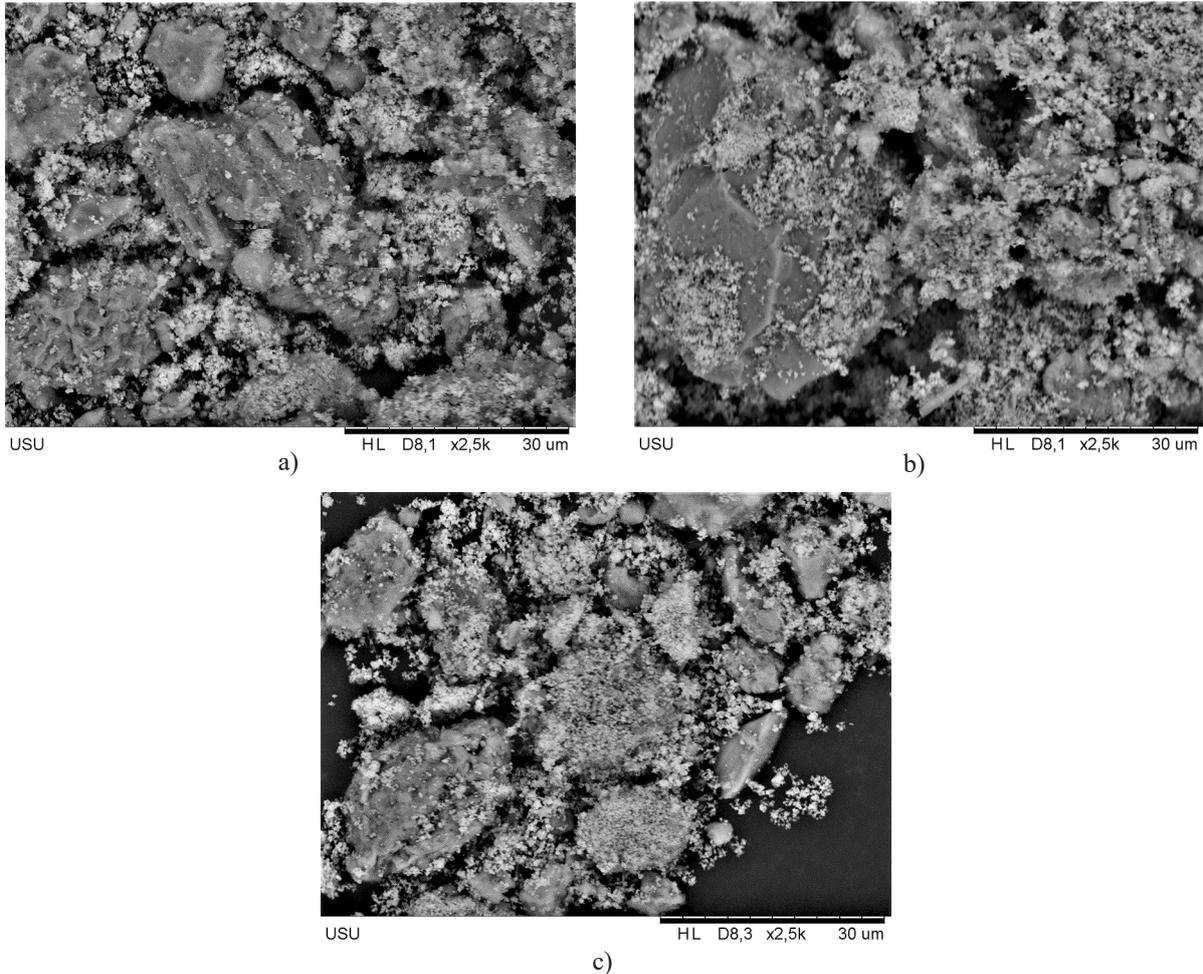


Fig. 2. XRD adsorbent: (a) OPBA/Bentonite/ TiO_2 (0:25:25 g), (b) OPBA/Bentonite/ TiO_2 (10:25:25 g), (c) OPBA/Bentonite/ TiO_2 (0:15:25 g)

Table 1. XRD adsorbent data

| XRD Data | OPBA/Bentonite/TiO ₂ (0:25:25 g) | OPBA/Bentonite/TiO ₂ (10:25:25 g) | OPBA/Bentonite/TiO ₂ (0:25:25 g) |
|----------------|--|--|---|
| Crystal system | Triclinic (anorthic) | Tetragonal | Tetragonal |
| Space group | P -1 | I 41/a m d | I 41/a m d |
| Unit cell | a = 5.4234 Å b = 7.1310 Å c = 14.7850 Å α = 98.442° β = 94.579° γ = 90.009° | a = 3.7800 Å c = 9.5100 Å | a = 3.7845 Å c = 9.5143 Å |
| Density | 4.017 g/cm ³ | 3.904 g/cm ³ | 3.894 g/cm ³ |

**Fig. 3.** Morphology of Adsorbent: (a) OPBA/Bentonite/TiO₂ (0:25:25 g), (b) OPBA/Bentonite/TiO₂ (10:25:25 g), (c) OPBA/Bentonite/TiO₂ (0:15:25 g)

On the basis of the data in Table 2, it can be seen that the addition of OPBA into Bentonite/TiO₂ causes a decrease in specific surface area. There are two factors which cause a decrease in area specific surface, the first caused by the sintering process OPBA particles on the surface external and internal montmorillonite. Sintering is merging particles at high temperature (calcination 500°C for 3 hours). The second factor is closure

of interlayer by OPBA particles. A decrease in specific surface area after OPBA dispersion occurs because OPBA enters the existing pores or partially covers them. Bentonite/TiO₂ surface so that OPBA covers the open pores. A decrease in the specific surface area can also result in reduced the adsorption ability of the material, however OPBA/Bentonite/TiO₂ composites have semiconductor properties that may be more dominant than

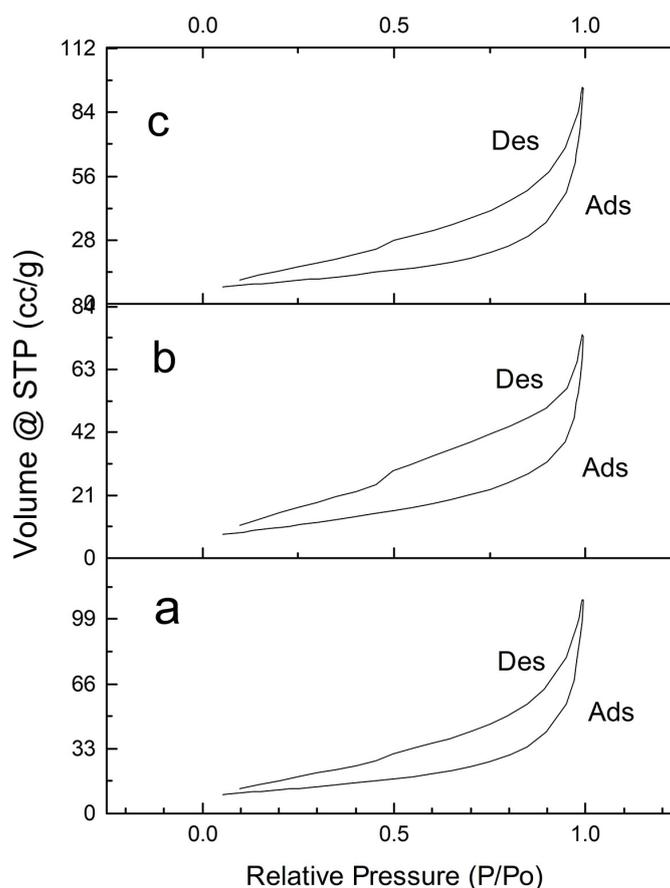


Figure 4. BET of adsorbent: (a) OPBA/Bentonite/TiO₂ (0:25:25 g), (b) OPBA/Bentonite/TiO₂ (10:25:25 g), (c) OPBA/Bentonite/TiO₂ (0:15:25 g)

Table 2. Data surface area, total pore volume, average pore radius of OPBA/Bentonite/TiO₂

| Sample | Surface area data | | Total pore volume (cc/g) | Average pore radius (Å) |
|--|--------------------------------------|---|--------------------------|-------------------------|
| | Single point BET (m ² /g) | Langmuir surface area (m ² /g) | | |
| OPBA/Bentonite/TiO ₂ (0:25:25 g) | 40.168 | 60.775 | 1.657 x 10 ⁻¹ | 70.909 |
| OPBA/Bentonite/TiO ₂ (10:25:25 g) | 30.670 | 60.308 | 1.143 x 10 ⁻¹ | 60.110 |
| OPBA/Bentonite/TiO ₂ (15:25:25 g) | 30.372 | 50.661 | 1.461 x 10 ⁻¹ | 80.555 |

the area reduction factor the surface, so that ability to degrade organic compounds will be higher. The average pore radius increased when the OPBA composition was 15 g. It can be seen that the pore size of the entire sample at the mesoporous region (Huang et al., 2017; Mirzapour et al., 2021; Saraswati & Nugraha, 2014).

CONCLUSIONS

The adsorbent spectra did not show a significant shift in absorption where the O-H bonds

were becoming weaker due to the presence of TiO₂ in the interlayer of bentonite. Another possibility is due to the influence of calcination and heating. The O-H groups of H₂O are hydroxylated and dehydrated between layers. The formation of the composite OPBA/TiO₂/Bentonite does not change the crystallinity of TiO₂ significantly. This proves that there is no decrease in photocatalyst activity after the addition of OPBA and bentonite. The morphology of the whole sample has a flake-like structure that has pores. The addition of OPBA into Bentonite/TiO₂ causes a decrease in the specific surface area of the sample.

Acknowledgments

This research was funded by Directorate General of Higher Education, Research and Technology. Ministry of Education, Research Culture, and Technology according to Number 036/E5/PG.02.00.PT/2022 and Number 001/UN33.8/DRTPM/PL/2022

REFERENCES

- Abdul Khalil, H.P.S., Marlina, M.M., Alshammari, T. 2011. Material properties of epoxy-reinforced biocomposites with lignin from empty fruit bunch as curing agent. *BioResources*. <https://doi.org/10.15376/biores.6.4.5206-5223>
- Basuki, K.T., Hasnowo, L.A., Jamayanti, E. 2019. Adsorption Of Uranium Simulation Waste Using Bentonite: Titanium Dioxide. *Urania Jurnal Ilmiah Daur Bahan Bakar Nuklir*. <https://doi.org/10.17146/urania.2019.25.1.4527>
- Bukit, B.F., Frida, E., Humaidi, S., Sinuhaji, P. 2022a. Preparation and characterization of CTAB surfactant modified TiO₂ nanoparticles as antibacterial fabric coating material. *Journal of Physics: Conference Series*, 2165(1), 012022. <https://doi.org/10.1088/1742-6596/2165/1/012022>
- Bukit, B.F., Frida, E., Humaidi, S., Sinuhaji, P. 2022b. Selfcleaning and antibacterial activities of textiles using nanocomposite oil palm boiler ash (OPBA), TiO₂ and chitosan as coating. *South African Journal of Chemical Engineering*, 41(February), 105–110. <https://doi.org/10.1016/j.sajce.2022.05.007>
- Bukit, B.F., Frida, E., Humaidi, S., Sinuhaji, P., Bukit, N. 2022. Optimization of Palm Oil Boiler Ash Biomass Waste as a Source of Silica with Various Preparation Methods, 23(8), 193–199.
- Bukit, N., Ginting, E.M., Frida, E., Bukit, B.F. 2021. Physical analysis of TiO₂ and bentonite nanocomposite as adsorbent materials. *Reviews on Advanced Materials Science*, 60(1), 912–920. <https://doi.org/10.1515/rams-2021-0076>
- Bukit, N., Ginting, E. M., Hutagalung, E.A., Sidebang, E., Frida, E., Bukit, B.F. 2019. Preparation and characterization of oil palm ash from boiler to nanoparticle. *Reviews on Advanced Materials Science*, 58(1), 195–200. <https://doi.org/10.1515/rams-2019-0023>
- Bukit, N., Ginting, E.M., Pardede, I.S., Frida, E., Bukit, B.F. 2018. Mechanical properties of composite thermoplastic hdpe / natural rubber and palm oil boiler ash as a filler. *Journal of Physics: Conference Series*, 1120(1). <https://doi.org/10.1088/1742-6596/1120/1/012003>
- Chun, H., Yizhong, W., Hongxiao, T. 2001. Preparation and characterization of surface bond-conjugated TiO₂/SiO₂ and photocatalysis for azo dyes. *Applied Catalysis B: Environmental*, 30(3–4), 277–285. [https://doi.org/10.1016/S0926-3373\(00\)00237-X](https://doi.org/10.1016/S0926-3373(00)00237-X)
- Đukić, A.B., Kumrić, K.R., Vukelić, N.S., Stojanović, Z.S., Stojmenović, M.D., Milošević, S.S., Matović, L.L. 2015. Influence of ageing of milled clay and its composite with TiO₂ on the heavy metal adsorption characteristics. *Ceramics International*, 41(3), 5129–5137. <https://doi.org/10.1016/j.ceramint.2014.12.085>
- Fatimah, I. 2012. Composite of TiO₂-montmorillonite from indonesia and its photocatalytic properties in methylene blue and e.coli reduction. *Journal of Materials and Environmental Science*.
- Frida, E., Bukit, N., Bukit, F.R.A., Bukit, B.F. 2022. Preparation and characterization of Bentonite-OPBA nanocomposite as filler. *Journal of Physics: Conference Series*, 2165(1). <https://doi.org/10.1088/1742-6596/2165/1/012023>
- Frida, E., Rahmat, F., Bukit, A., Bukit, F. 2022. Analysis Structure and Morphology of Bentonite-Opba. 20, 117–125.
- Ginting, E.M., Bukit, N., Frida, E., Bukit, B.F. 2020. Microstructure and thermal properties of natural rubber compound with palm oil boilers ash for nanoparticle filler. *Case Studies in Thermal Engineering*, 17, 100575. <https://doi.org/10.1016/j.csite.2019.100575>
- Ginting, E.M., Bukit, N., Motlan, Saragih, M.T., Frida, E., Bukit, B.F. 2020. Analysis of natural rubber compounds with filler of Oil Palm Empty Bunches Powder and Carbon Black. *Journal of Physics: Conference Series*, 1428(1). <https://doi.org/10.1088/1742-6596/1428/1/012024>
- Ginting, E.M., Bukit, N., Muliani, Frida, E. 2017. Mechanical properties and morphology natural rubber blend with bentonit and carbon black. *IOP Conference Series: Materials Science and Engineering*. <https://doi.org/10.1088/1757-899X/223/1/012003>
- Huang, Z., Li, Y., Chen, W., Shi, J., Zhang, N., Wang, X., Li, Z., Gao, L., Zhang, Y. 2017. Modified bentonite adsorption of organic pollutants of dye wastewater. *Materials Chemistry and Physics*, 202, 266–276. <https://doi.org/10.1016/j.matchemphys.2017.09.028>
- Ibrahim, S.A., Sreekantan, S. 2011. Effect of pH on TiO₂ nanoparticles via sol-gel method. *Advanced Materials Research*, 173. <https://doi.org/10.4028/www.scientific.net/AMR.173.184>
- Khanday, W.A., Asif, M., Hameed, B.H. 2017. Cross-linked beads of activated oil palm ash zeolite/chitosan composite as a bio-adsorbent for the removal of methylene blue and acid blue 29 dyes.

- International Journal of Biological Macromolecules. <https://doi.org/10.1016/j.ijbiomac.2016.10.075>
20. Liu, C., Zhang, R., Wei, S., Wang, J., Liu, Y., Li, M., Liu, R. 2015. Selective removal of H₂S from biogas using a regenerable hybrid TiO₂/zeolite composite. *Fuel*. <https://doi.org/10.1016/j.fuel.2015.05.003>
21. Lubis, K., Frida, E., Sebayang, K., Sinuhaji, P., Humaidi, S., Fudholi, A. 2022. The development of a novel FM nano-adsorbent for heavy metal remediation in polluted water. *South African Journal of Chemical Engineering*, 39, 32–41. <https://doi.org/10.1016/j.sajce.2021.11.006>
22. Manikam, M.K., Halim, A.A., Hanafiah, M.M. 2019. Pollutants removal from sewage wastewater using palm oil fuel ash. *AIP Conference Proceedings*. <https://doi.org/10.1063/1.5111270>
23. Manikam, M.K., Halim, A.A., Hanafiah, M.M., Krishnamoorthy, R.R. 2019. Removal of ammonia nitrogen, nitrate, phosphorus and cod from sewage wastewater using palm oil boiler ash composite adsorbent. *Desalination and Water Treatment*. <https://doi.org/10.5004/dwt.2019.23842>
24. Mirzapour, P., Kamyab Moghadas, B., Tamjidi, S., Esmaili, H. 2021. Activated carbon/bentonite/Fe₃O₄ nanocomposite for treatment of wastewater containing Reactive Red 198. *Separation Science and Technology (Philadelphia)*, 56(16), 2693–2707. <https://doi.org/10.1080/01496395.2020.1843051>
25. Saraswati, A., Nugraha, I. 2014. Seminar Nasional Kimia Dan Montmorillonit-TiO₂ Dan. Seminar Nasional Kimia Dan Pendidikan Kimia VI.
26. Sirait, M., Bukit, N., Siregar, N. 2017. Preparation and characterization of natural bentonite in to nanoparticles by co-precipitation method. *AIP Conference Proceedings*, 1801. <https://doi.org/10.1063/1.4973084>
27. Sirait, M., Gea, S., Bukit, N., Siregar, N., Sitorus, C. 2018. Synthesis of nanobentonite as heavy metal adsorbent with various solvents. *Oriental Journal of Chemistry*, 34(4), 1854–1857. <https://doi.org/10.13005/ojc/3404020>
28. Sutrisno, B., Hidayat, A., Mufrodi, Z. 2016. Modifikasi Limbah Abu Layang menjadi Adsorben untuk Mengurangi Limbah Zat Warna pada Industri Tekstil. *CHEMICA: Jurnal Teknik Kimia*. <https://doi.org/10.26555/chemica.v1i2.3571>
29. Toor, M., Jin, B., Dai, S., Vimonses, V. 2015. Activating natural bentonite as a cost-effective adsorbent for removal of Congo-red in wastewater. *Journal of Industrial and Engineering Chemistry*. <https://doi.org/10.1016/j.jiec.2014.03.033>
30. Wang, F.Y., Wang, H., Ma, J.W. 2010. Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent-Bamboo charcoal. *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2009.12.032>
31. Zhuang, W., Zhang, Y., He, L., An, R., Li, B., Ying, H., Wu, J., Chen, Y., Zhou, J., Lu, X. 2017. Facile synthesis of amino-functionalized mesoporous TiO₂ microparticles for adenosine deaminase immobilization. *Microporous and Mesoporous Materials*, 239, 158–166. <https://doi.org/10.1016/j.micromeso.2016.09.006>
32. Zuo, S., Ding, M., Tong, J., Feng, L., Qi, C. 2015. Study on the preparation and characterization of a titanium-pillared clay-supported CrCe catalyst and its application to the degradation of a low concentration of chlorobenzene. *Applied Clay Science*. <https://doi.org/10.1016/j.clay.2014.12.033>