# Novel spent bleaching earth industrial waste as low-cost ceramic membranes material: elaboration and characterization

*by* Ahmad Saiful Haqqi

---

ARTICLE IN PRESS

Materials Today: Proceedings xxx (xxxx) xxx

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

# Novel spent bleaching earth industrial waste as low-cost ceramic membranes material: elaboration and characterization

Aulia Rahma [a,d], Muthia Elma [a,b,d,*], Muhammad Roil Bilad [c], Isnasyauqiah [a,b], Abdul Rahman Wahid [b,d], Muhammad Sirajul Huda [b,d], Dwi Resa Lamandau [b,d]

[a] Doctoral Program of Environemntal Science, Postgraduate Program, Lambung Mangkurat University, Jl Brigjen H. Hasan Basri, Kayutangi, Banjarmasin 70123, South Kalimantan, Indonesia
[b] Chemical Engineering Department, Engineering Faculty, Lambung Mangkurat University, Jl A. Yani Km 36, Banajrbaru 70714, South Kalimantan, Indonesia
[c] Faculty of Integrated Technologies, Universiti Brunei Darussalam, Gedung BE1410, Brunei
[d] Materials and Membranes Research Group (M²ReG), Lambung Mangkurat University, Jl A. Yani Km 36, Banajrbaru 70714, South Kalimantan, Indonesia

ARTICLE INFO

*Article history:*
Available online xxxx

*Keywords:*
SBE
Ceramic membrane
Support
Pressing method
CPO

ABSTRACT

Ceramic membrane support derived from spent bleaching earth (SBE) become a novel study due to their low-cost, sustainable features, abundance material, and there is not yet applicated as membrane. In this study, flat disk ceramic membrane configuration was fabricated and characterized from solid waste of crude palm oil bleaching process by pressing method in different SBE loading mass (38–42 %wt.). The SBE as raw material was deoiled using n-hexane and acetone solvent, followed by fabricated it become flat disk SBE membranes. Afterward, the SBE flat disk membranes was characterized through fourier-transform infrared spectroscopy (FTIR) and X-ray fluorescence (XRF) analyzer. The result exhibits the flat disk SBE ceramic membrane has dimension of 41 and 6 mm for diameter and thickness, respectively. SBE membranes indicating have montmorillonite structure due to presence of silica as main component materials of SBE. Besides that, the existence of siloxane vibration band in SBE membranes for the sample after regeneration with n-hexane and acetone were dominated over using raw SBE. It concludes the oil residue was removed and produced SBE membrane properties become robust with less organic contaminant.



## 1. Introduction

Inorganic membranes have several advantages over polymeric membranes especially when applied for water and waste water treatment. For example the ceramic membranes were offering: (1) the resistance to extreme temperatures; (2) robust/stronger; and (3) resistant to certain fouling [1–7]. Apart from these advantages, the price of inorganic membranes is still relatively expensive if compared to polymer membranes. It is due to the cost of materials and the complex of manufactures [8–10]. To overcome this issue, researchers have been being conducted research in the manufacture of inorganic membranes with alternative materials that abundant and sustainable.

Several studies have been reported the success of making economical and strong inorganic membranes with their advantages fabricated from natural clay such as peat clay [11], Moroccan clay and kaolin [12–14]. Ceramic membrane also have been reported derived from industrial waste such as fly ash [15–18] and other silica, alumina based materials [19]. Meanwhile, another material from industrial waste that abundant available is spent bleaching earth (SBE). The SBE is a waste that generates from the refining of crude palm oil (CPO). In Indonesia, there are more than 100,000 tons per year of SBE is being produced [20].

More than 2 million tons per year of SBE is produced worldwide with large quantities available in the Middle East where significant volumes of vegetable oil are produced [21]. In the oil industry, SBE is commonly used to treat and remove toxins and dyes from crude oil [22]. SBE is mainly composed of clay minerals such as bentonite and smectite [23]. SBE is derived from bleaching earth (bentonite

* Corresponding author.
*E-mail address:* melma@ulm.ac.id (M. Elma).

https://doi.org/10.1016/j.matpr.2023.02.387
2214-7853/

Please cite this article as: A. Rahma, M. Elma, M. Roil Bilad et al., Novel spent bleaching earth industrial waste as low-cost ceramic membranes material: elaboration and characterization, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2023.02.387

clay) which refers to natural or active clay that has the capacity to absorb colored materials and other impurities during the oil refining process [24]. Bentonite clay consists of 0.96% CaO, 69.8% $SiO_2$ and 11.88% $Al_2O_3$ [25].

The bleaching earth itself is a kind of clay with the main composition consisting of $SiO_2$, $Al_2O_3$, $Fe_2O_3$, CaO, and MgO which is used for the adsorption process of color components in vegetable oils. [26]. So far, SBE waste has not been widely used and is usually disposed of in landfills and due to the high cost of disposal, this material needs to be used [27].

Fabrication of membranes are from the different materials such as ceramics, polymers, metals and/or glass [28–30]. The high content of oxide compounds such as alumina and silica in SBE was potential to be elaborated into ceramic membranes. Furthermore, the thermal stability ensures that the membrane is ideal for applications at high temperatures. In addition, ceramic membranes are less susceptible to microbial attack and biological degradation [31–32]. As a result, porous ceramic membranes have different industrial applications in areas such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), to concentrate or separate some compounds from water or other liquids in areas such as: food industry, textiles, pharmaceuticals, chemicals or leather [33–34]. The disadvantages of using ceramic membranes are that they are ten times more expensive than polymer membranes, their incompatibility with alkalis, and the brittleness of ceramic materials, which brings certain difficulties to the membrane formation and assembly process. [35]. For this reason many researchers have reported the manufacture of membrane ceramics using cheaper, natural, and abundant raw materials such as dolomite, attapulgite, and natural clay. [36]. Meanwhile, the development of inorganic membranes based on natural materials such as clay has been investigated by several authors Alreheedi and Basu 2014 [37], Elma et al. 2016 [38], Sarkar et al. 2012 [39], Vercauteren et al. 1996 [40], Zhang, Luo, and Zhang 2012 [41]. However, until now there has been no research related to the utilization of SBE waste as a material for making ceramic membranes. The consideration of cheap raw material prices and the combustion process at a lower temperature so that it can be applied as a raw material for the manufacture of membrane support is a separate value in the ceramic membrane processing process.

In other place such as Japan, SBE has been incinerated for cement manufacturing. Unfortunately, there are several difficulties found in maintaining good cement quality due to the high concentration of oil in the material [42]. This research is trying to convert SBE into a more valuable material becomes indispensable [43]. So far, SBE is still applied as an adsorbent and mixing material for concrete, brick, and asphalt [44] and there is no publication reports yet for SBE applied as membrane support. Based on this background, it can be concluded that the material for making porous ceramics from SBE containing silica and alumina can be used as an alternative as raw material for making membrane support. The aims of this study is to prepare groups and characterize the novel industrial waste-derived low-cost ceramic membranes from spent bleaching earth into plate disk configuration. Furthermore, the functional of SBE ceramic membranes were examined using fourier-transform infrared spectroscopy (FTIR).

## 2. Materials and methods

### 2.1. Chemicals and materials

The preparation of novel derived industrial waste ceramic membranes was conducted using spent bleaching earth (SBE) as raw materials (specification Taiko bleaching earth Sdn Bhd, Malaysia), which collected from PT. Sime Darby Oil, Pulau Laut South Kalimantan-Indonesia. n-hexane and acetone (technical grade) were purchased from local suppliers PT. Tunggal Jaya Kimia, Surabaya-Indonesia. While other chemical agent PEG-400, CMC (carboxymethyl cellulose) and methyl cellulose as plasticizer and binder were acquired from local company PT. Sumber Kita Indah, Bekasi-Indonesia.

### 2.2. Preparation of raw materials

The SBE as raw material was deoiled by mixed SBE with varied solvent i.e., n-hexane (1:3 wt% of SBE:n-hexane) and acetone (1:2 wt% of SBE:acetone). SBEs were stirred at 300 rpm at 40 °C for 30 min then followed by centrifuged the solution at 4000 rpm for 30 min. The sediment was dried in oven at 100 °C for an hour, and then sieved to a fine powder with mesh size 100 µm. The fines SBE was calcined at 550 °C for 4 h, afterward samples were analyzed using Fourier-transform infrared spectroscopy (Bruker Alpha FT-IR) to identification of functional groups present in SBE. X-ray fluorescence (XRF) to analyze the chemical composition or elements present in the sample using ARL 9900 of Thermo Fisher.

### 2.3. Preparation and characterization of SBE membranes

The preparation of flat disk support membrane was done in three steps: (1) the preparation of paste mixed from fines SBE with a plasticizer and binding additives in demineralized water; (2) pressing method of the sample; and (3) consolidation by thermal treatment of the obtained flat disk. The formulation of the SBE ceramic support contains (values are given in %wt.) as follows on Table 1.

The paste was prepared form slow mixture of deoiled SBE and organic additives in varied formulation, and the mixture was homogenized with addition of water. The paste is presented using hydraulic pressure at 4–7 MPa with flat disk mold, as shows on Fig. 1. After aging for 12 h at room temperature (25 °C) to ensure a homogeneous drying and hinder bending, it was then dried at 100 °C for 12 h using oven. Each flat disk obtained had 41 mm diameter and thickness of 6 mm. Finally, the SBE flat disk ceramic membranes were sintering to improve the porosity. Programable furnace was used for sintering process due to avoid thermal stress in SBE membrane structure. In the first stage, the SBE ceramic membrane was sintered with a heating rate of 2 °C.min$^{-1}$ until 800 °C, and hold at the same temperature for 2 h. The cooling rate was set naturally degradation. Visual characterization was observed by the size of external diameter and thickness of membrane during the sintering process. After thermal treatment, the diameter of each support decreases, which is due to the presence of shrinkage phenomena. Fourier-transform infrared spectroscopy (Bruker Alpha FT-IR) was used to analyzed the functional groups present in SBE ceramic membrane.

## 3. Results and discussion

FTIR spectra were analyzed to investigate the surface characteristic of SBE as membrane material at wavenumber range 4000–700 cm$^{-1}$ as shown in Fig. 2. The result shows FTIR spectra of SBE in varied pretreatment using multiple solvent indicated that there are siloxane (Si–O–Si) peak band at wavenumber 1020–1075 cm$^{-1}$. Whereas, at wavenumber 1730–1740 cm$^{-1}$ exhibits functional groups of ester (C=O). Furthermore, at 2850–2950 cm$^{-1}$ band indicated functional group of hydrogen carbon (C–H) [45]. The theorical stretching vibrations of different –OH groups resent in Mg–OH–Al, Al–OH–Al, and Fe–OH–Al units in

**Table 1**
The formulation of SBE ceramic support.

| Samples | SBE | CMC | PEG | Methyl cellulose | $H_2O$ |
|---|---|---|---|---|---|
| SBE-A | 38 | 4 | 3 | 4 | 51 |
| SBE-B | 40 | 4 | 3 | 4 | 49 |
| SBE-C | 42 | 4 | 3 | 4 | 47 |

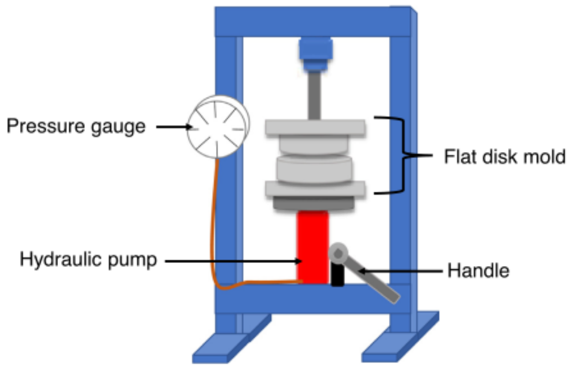


**Fig. 1.** Schematic of manual hydraulic pump for membrane pressing.

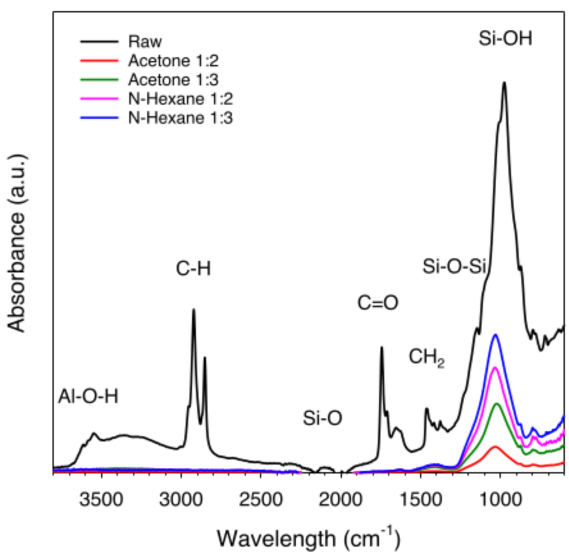


**Fig. 2.** Infrared spectra of raw SBE and varied solvent for deoiled SBE materials.

the octahedral layer were observed at 3000 $cm^{-1}$ in raw SBE sample [46].

Fig. 2 SBE Performance after pretreatment using both n-hexane and acetone have Si–O–Si band more clearly than raw material sample. It is due to the solvent and pretreatment were increasing silica purification in raw SBE samples. In calcination process at over 500 °C is able to degradate organic and residue contaminant from SBE raw materials. It is proved by the absorbance of other functional group peaks did not detected anymore [47].

XRF results from raw and deoiled SBE samples that have been regenerated using n-hexane (1:3 wt%) as solvent are presented in Table 2. It can be seen from the table that the highest chemical element content of raw SBE is $SiO_2$ then followed by $Al_2O_3$. The results exhibit the domiation of silica and alumina in SBE is indicated that material suitable to produce ceramic support membrane. It is important to know the chemical compositions of the minerals that are existence in the SBE. In XRF method, fluorescent X-rays are emitted from a material that has been excited by bombarding with high-energy x-rays. Based on Table 2 displays that the SBE was made up of silica, alumina, calcium, sodium, magnesium, and iron oxides in major quantities and other elements in trace amounts.

The addition of organic additives (Table 1) such as metochel, carboxy methyl cellulose (CMC) and the concentration of water on SBE greatly affected the shape of the plastic mass produced (Fig. 3). Fig. 3 shows the composition of the same additive mixture with different SBE mass mixing (38–42%). The greater the mass of SBE added, the more difficult it will be to homogenize the SBE mixture with the addition of other additive compositions. The arrow to the right shows the increasing mass of SBE, and this indicates that the plasticity of the mixture will be more visible and not flatten.

Fig. 4 (a) shows SBE ceramic membrane after pressing into flat disk configuration after aged and dried by oven, while Fig. 4 (b) membrane after sintering by programable furnace. However, the ceramic membrane with SBE 38 loading after sintered not available in the present Fig. 4 due to the membrane was cracked. It is due the SBE-A membrane has high of water and bring out the porosity of ceramic support become fragile over SBE-B and SBE-C samples. The result obtained SBE ceramic membranes diameter were drecreased <0.041 m due to the shrinkage effect [48]. Nevertheles, the flat disk membrane still have good shapes as displays in Fig. 4. The SBE ceramic membrane has asymetric character and brick light color.

The characterization of membranes that have passed the extrusion process aims to determine the density of the matrix groups and functional groups contained in the membrane material. Prior to the characterization using Fourier Transform Infra - Red (FTIR), a mixture of SBE and other organic additives was sintered. In this sintering stage, the particles in the porous ceramic combine to form aggregates that have high mechanical strength [49]. The presence of oxides of alkali and alkaline earth metals in porous ceramics can increase the speed of sintering by forming a liquid that can pull the granules together by surface tension forces so that the shape of the porous ceramic will experience shrinkage and increase in density [50].

The functionalization of the calcined SBE material using a mixture of additives was tested by FTIR with a wavenumber range of 600 to 3000 $cm^{-1}$ as shown in Fig. 5. After the FTIR test, it was found that there were siloxane groups (Si–O–Si) in the material, especially the band near 1020–1075 $cm^{-1}$. It shows the SBE samples have monthmorillonite structure which is similar to the fuctionalization result of SBE material from previous work [51]. The results of the FTIR test (Fig. 5) show that there are differences in each peak between the membrane samples that have gone through the calcination process with different SBE compositions. All membrane sample show siloxane and silanol vibration band as similar to other work that prepare inorganic (silica based) membrane [52–57]. Sample 1 shows a very clear peak compared to the peaks found in other samples at the same wavenumber.

**Table 2**
Chemical analysis of SBE using XRF.

| Chemical composition | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $K_2O$ | $Na_2O$ | $TiO_2$ | $Cl^-$ | Another compound |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Raw SBE (wt%) | 44.97 | 7.54 | 3.23 | 8.31 | 3.92 | 1.96 | 2.24 | 6.18 | 1.03 | 7.20 | 13.42 |
| Deoiled SBE using n-hexane 1:3 (wt%) | 47.89 | 9.67 | 7.42 | 7.35 | 6.54 | 0.65 | 2.39 | 9.93 | 0.87 | 0 | 7.29 |

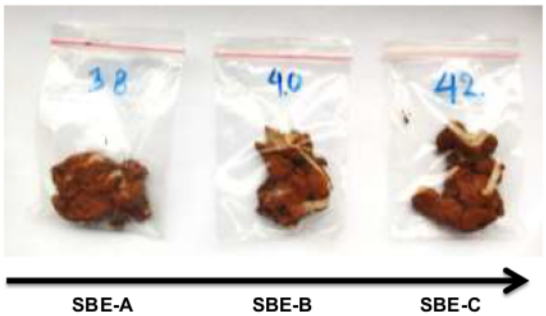


**Fig. 3.** SBE paste after mixing with additives with different SBE loading (wt%).

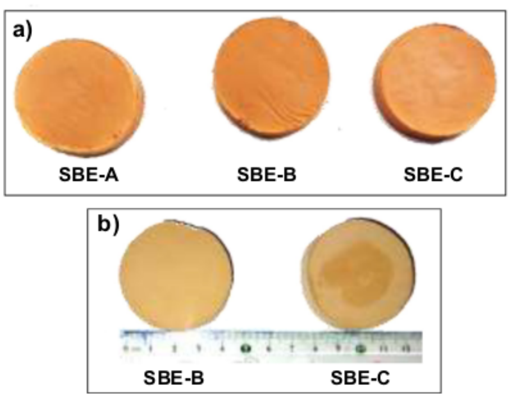


**Fig. 4.** (b) SBE ceramic membrane flat disk after aged and dried at 100 °C, while (b) SBE membrane after sintering at 800 °C.

## 4. Conclusion

Low-cost ceramic membrane support was successfully fabricated from SBE via pressing method in flat disk configuration. Regeneration SBE material using varied solvent (n-hexane and acetone) exhibited $SiO_2$ component increases due to the organic residue contaminant well removed. The fabricated of SBE ceramic membrane excellent prepared and shaped into flat disk configuration with different SBE mass loading. The chemical properties of the SBE membranes support are indicating by the existence of Si–O–Si (siloxane) vibration group and Si–O–Al on all membrane properties. It concluded that ceramic membranes prepared from SBE has montmorillonite structure with less organic contaminant and able for future application as membrane support in separation process.

## CRediT authorship contribution statement

**Aulia Rahma:** Conceptualization, Methodology, Software, Validation, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. **Muthia Elma:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Muhammad Roil Bilad:** Conceptualization, Formal analysis, Investigation, Writing – original draft, Visualization, Supervision. **Isnasyauqiah:** Formal analysis, Investigation, Writing – original draft, Visualization, Supervision. **Abdul Rahman Wahid:** Resources, Data curation, Writing – original draft, Visualization. **Muhammad Sirajul Huda:** Resources, Data curation, Writing – original draft, Visualization. **Dwi Resa Lamandau:** Resources, Data curation, Writing – original draft, Visualization.

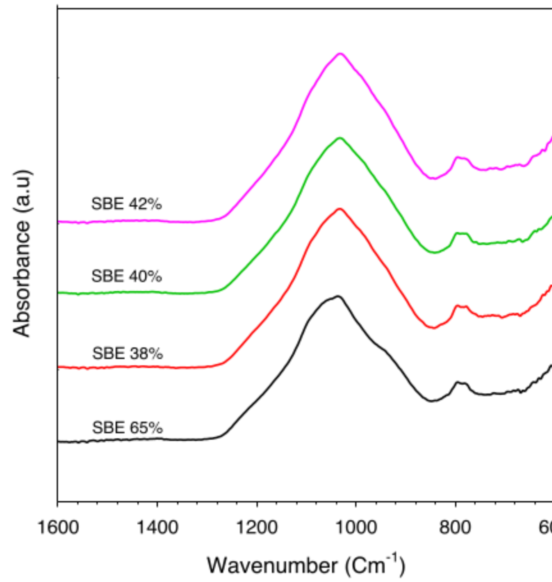


**Fig. 5.** Infrared spectra of ceramic membranes with multiple SBE loading, black line for SBE membrane without additives.

## Data availability

Data will be made available on request.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

Authors thanks to Materials and Membranes Research Group ($M^2$ReG) for the facilities provided. Muthia also thanks to Applied Research Universities Grant 2021-2023, Thesis and Dissertation Grant 2022 The Ministry of Research and Technology / National

Research and Innovation Agency, The Ministry of Education and Culture of the Republic of Indonesia.

## References

[1] M. Elma et al., J. Water Process Eng. 38 (2020).
[2] M. Elma et al., J. Adv. Res. Fluid Mech. Therm. Sci 100 (1) (2022) 77.
[3] M. Elma et al., Sustainability 14 (1) (2022) 370.
[4] M. Elma et al., Organosilica Multichannel Membranes Prepared by Inner Coating Method Applied for Brackish Water Desalination, in: Materials Science Forum, Trans Tech Publ., 2022, vol. 1057, p. 136.
[5] M. Elma et al., Polymers 14 (5) (2022) 895.
[6] M. Elma et al., J. Adv. Res. Fluid Mech. Therm. Sci. 100 (2) (2022) 33.
[7] R. Aulia et al., J. Adv. Res. Fluid Mech. Therm. Sci. 100 (3) (2022) 133.
[8] S. Satria Anugerah et al., J. Adv. Res. Fluid Mech. Therm. Sci. 101 (2) (2022) 46.
[9] A. Rahma et al., Membr. Technol. 2022 (2022) 3.
[10] N.I. Mat Nawi et al., Membranes 12 (6) (2022) 554.
[11] M. Elma et al., Teknoin 22 (2016) 6.
[12] M. Purnima et al., Sep. Purif. Technol. 250 (2020).
[13] A. Agarwal et al., J. Pet. Sci. Eng. 194 (2020).
[14] A. Elgamouz et al., Heliyon 5 (8) (2019) e02281.
[15] K.P. Goswami et al., Sci. Total Environ. 808 (2022).
[16] R. Chathurappan, J. Anandkumar, Materialia (2022) 101548.
[17] C. Wang et al., Ceram. Int. 47 (16) (2021) 22302.
[18] B. Ahmad et al., Int. J. Environ. Sci. Technol. (2021).
[19] F. Azaman et al., Malays. J. Fundam. Appl. Sci 17 (2021) 62.
[20] N. Hindryawati et al., J. Bahan Alam Terbarukan 6 (1) (2017) 68.
[21] A. Beshara, C.R. Cheeseman, Waste Manage. J. (2014) 5.
[22] M. Malakootian et al., Desalination 277 (2011) 244.
[23] D. Karadag et al., J. Hazard. Mater. 144 (2007) 432.
[24] M.R. Sabour, M. Shahi, Civil Eng. J. 4 (2018) 584.
[25] M.R. Sabour, M. Shahi, Civil Eng. J. 4 (2017) 13.
[26] M. Saputri, V.L. Riyandini, J. Aerasi 2 (2020) 1.
[27] S.K. Loh et al. (2013) 49, 775.
[28] S.T. Kassa et al., Surface Coat. Technol. J. 368 (2019) 33.
[29] B. Zhu et al., Short Review on Porous Metal Membranes—Fabrication, Commercial Products, and Applications, Victoria University, Melbourne, Australia, Institute for Sustainable Industries and Liveable Cities, 2018, p. 1.
[30] D. Sun et al., J. Membr. Sci. 146 (1998) 65.
[31] D. Liang et al., Ceram. Int. J. 47 (2021) 10464.
[32] J. Wehling et al., Mater. Sci. Eng. C J. (2015) 179.
[33] A. Abdullayev et al., Materials and Applications for Low-Cost Ceramic Membranes, Technische Universität Berlin, Berlin, Germany, Institute of Materials Science and Technology, 2019, p. 1.
[34] D. Vasanth et al., J. Membr. Sci. 379 (2011) 154.
[35] F. Lin et al. (2018) 4.
[36] N. Kamoun et al. (2020), 393.
[37] M.T. Alresheedi, O.D. Basu, J. Membr. Sci. (2014) 450.
[38] M. Elma et al., Teknoin 22 (2016) 443.
[39] S. Sandeep et al., J. Membr. Sci. (2012) 392.
[40] S. Vercauteren et al., J. Membr. Sci. (1996) 119.
[41] Zhang Lichao et al. (2012) 406.
[42] E.Y. Park et al., J. Am. Oil Chem. Soc. 81 (1) (2004) 57.
[43] L.S. Kheang et al., Residual Oil from Spent Bleaching Earth (sbe) for Biodiesel and Biolubricant Applications, 2007.
[44] R. Othman et al., Eur. J. Environ. Civ. Eng. (2020) 1.
[45] W. Liu et al., Environ. Sci. Pollut. Res. 28 (1) (2021) 711.
[46] R. Chihi et al., C. R. Chim. 22 (2–3) (2019) 188.
[47] A. Merikhy et al., Chem. Eng. Process. - Process Intesif. 158 (2020).
[48] N. Kamoun et al., Boletín de la Sociedad Española de Cerámica y Vidrio 59 (1) (2020) 25.
[49] J.S. Reed, Principles of Ceramics Processing, John Wiley & Sons New York, 1995.
[50] J.T. Jones, M.F. Berard, Ceramic Industrial Processing and Testing, Lowa State University Press, 1993
[51] A. Yulikasari et al., J. Ecol. Eng. 23 (4) (2022) 96.
[52] A. Rahma et al., Membr. Technol. 2020 (6) (2020) 7.
[53] Mahmud, et al., Mater. Sci. Forum 988 (2020) 114.
[54] R.A. Lestari et al., E3S Web Conf. 148 (2020) 07006.
[55] M. Elma et al., Asia Pac. J. Chem. Eng. (2020), n/a (n/a), e2461.
[56] M. Elma et al., Mater. Sci. Forum 981 (2020) 349.
[57] M. Elma et al., Polymers 12 (11) (2020) 2644.

# Novel spent bleaching earth industrial waste as low-cost ceramic membranes material: elaboration and characterization

ORIGINALITY REPORT

| 13% | 6% | 13% | 6% |
| --- | --- | --- | --- |
| SIMILARITY INDEX | INTERNET SOURCES | PUBLICATIONS | STUDENT PAPERS |

MATCH ALL SOURCES (ONLY SELECTED SOURCE PRINTED)

10%

★ Muthia Elma, Ni Kadek Devi Ananda Saraswati, Paskah Fransiska Afrida Simatupang, Retno Febriyanti et al. "Hydrogel derived from water hyacinth and pectin from banana peel as a membrane layer", Materials Today: Proceedings, 2023

Publication

| | | | |
| --- | --- | --- | --- |
| Exclude quotes | Off | Exclude matches | < 2% |
| Exclude bibliography | On | | |