

# Removal of total dissolved solids from oil-field-produced water using ceramic adsorbents integrated with reverse osmosis

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and including South Sumatra region ranges from 100 mg/L to 400,000 mg/L which is also influenced by the age of the oil well, the location of the oil well, and geological variations between basins and water resources [8–11]. Some methods are available to reduce the TDS value in produced water, such as physical separation, reverse osmosis, distillation, precipitation, and electrocoagulation developed to decrease the TDS value in water and wastewater [12]. However, some of these methods require high costs for their implementation. For instance, the distillation process can produce water with low conductivity but requires high energy in their operation. Biological absorption method is carried out to avoid using chemicals, but the process is controlled by microbes activities [13]. Therefore, it is necessary to take a reasonable approach that can reduce the TDS value in produced water by using combined the adsorbent and membrane desalination.

The most frequently used desalination method is Reverse Osmosis (RO) membrane. The application of RO membranes in the PW treatment to reduce the TDS value has increased in the last decade. Reverse osmosis is a membrane separation technology for removing compounds including TDS and heavy metals in both water and wastewater. Decreasing TDS using RO membranes have advantages such as not requiring chemicals, low energy, and producing high-quality permeate water. However, RO is prone to fouling due to the presence of dissolved solids and suspended solids in the water and wastewater. The performance of RO is depending in the types of membrane materials. Nowadays, ceramic and polymers type membranes are available in the market. Ceramic membranes have advantages because of their mechanical strength, good thermal and chemical stability, and can be synthesized from various metal oxides [14–15]. However, their high costs material manufacturing, handling problem due to their brittleness, and difficulty in scale up become the main problems for the industrialization of ceramic membranes [16–17].

The catalytic cracking unit at the oil refinery in South Sumatra, Indonesia produces the residue of catalytic cracking (RCC) catalyst of approximately 15 tons per annum which is only stored and sent to the hazardous solid disposal site [15]. The spent catalyst of catalytic cracking residues contains silica and alumina which is the material of ceramic filters manufactured [18]. Therefore, the RCC is a potential material to be used as ceramic adsorbent for PW treatment. Ceramic adsorbents have advantages in water filtration because of their thermal and chemical stability [19]. In addition, their large surface area will have an advantage in adsorption of solid particle in water and wastewater. Natural clay is a colloidal soil particle that is finely shaped, containing aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and silicon dioxide ( $\text{SiO}_2$ ). Natural clay has advantages such as being abundantly available, low price, high specific surface area, high adsorption properties, and non-toxic [15]. The current investigation discusses the TDS removal by ceramic adsorbents from the mixture of spent catalyst RCC and natural clay in various composition integrated with RO in the treatment of produced water. The aims of the current work are to use an alternative method in the treatment of PW using low-cost ceramic adsorbent and reduce RO fouling potential in produced water treatment.

## 2. Materials and methods

The oil and gas industry in South Sumatra Province supplied the produced water samples. The initial characterization of produced water contains a total dissolved solids of 14,556 mg/L. This value exceeds the maximum permissible limit according to the Ministry of Environment and Forestry of Indonesia Regulation No. 5/2014, where the maximum allowable limit is 4000 mg/L for petroleum and gas exploration liquid waste. Ceramic adsorbents were made by a mixture of clay and spent catalyst of residue catalytic cracking

(RCC) unit at various composition. Clay cleaned from any impurities and dried at 100 °C in oven and grinded into powder with 100 mesh of particle size. The RCC with particle size of 100 mesh was dried in the furnace at 700–900 °C for one hour to remove hydrocarbon covered their surface. The mixture of clay and RCC was homogenized with demineralized water to form a paste. The paste mixture was molded to form a tablet of adsorbent with a diameter of 10 mm and 20 mm, respectively. All the adsorbents having thickness of 10 mm. The adsorbent mixture then dried in the oven for  $\pm 2$  h at 100 °C. In the next step, adsorbent mixture was calcinated in the furnace at 900 °C–1000 °C overnight. Ceramic adsorbent was removed from the furnace and an inspection is carried out if there are broken or cracked ceramic adsorbents to be separated. The selected of good ceramic adsorbent sample was subject to SEM-EDX and BET analysis.

The composition of ceramic adsorbents is determined as follows:

- Adsorbent A: 70% clay and 30% RCC with an adsorbent diameter of 10 mm
- Adsorbent B: 70% clay and 30% RCC with an adsorbent diameter of 20 mm
- Adsorbent C: 30% clay and 70% RCC with an adsorbent diameter of 10 mm
- Adsorbent D: 30% clay and 70% RCC with an adsorbent diameter of 20 mm

Fig. 1. Illustrates the photograph of ceramic adsorbent.

Research variable studied in the experiment are contact times (15, 30, 45, and 60 min) and flow rate of sample to adsorbent column (6, 7, and 8 L/min). The produced water is transferred using a centrifugal pump to a series of propylene sediment filters with pore sizes of 0.5, 0.3  $\mu\text{m}$ , and 0.1  $\mu\text{m}$ , respectively. The propylene sediment filter was cylindrical tube with length 254 mm and diameter of 65.5 mm. From the sediment filter column, produced water flows into the adsorption column. The adsorbate of the adsorption column is collected in a tank with a capacity of 500 L and pumped into RO membrane using a high-pressure pump. The RO membrane has length of 1016 mm and the diameter of 101 mm was use as the final treatment. RO permeate collected in the permeate tank and retentate are sent to the concentrate tank. The permeates were subject to TDS measurement using Thermo Scientific (EUTECH TN-100, TDS meter).

The TDS removal is calculated using the following equation.

$$\text{TDS Removal} = \frac{\text{TDS}_{\text{in}} - \text{TDS}_{\text{out}}}{\text{TDS}_{\text{in}}} \times 100\% \quad (1)$$

Where:  $\text{TDS}_{\text{in}}$  is the initial concentration of TDS (mg/L) and  $\text{TDS}_{\text{out}}$  is the final TDS concentration (mg/L).

The schematic of produced water treatment in this study is shown in Fig. 2.

## 3. Results and discussion

### 3.1. SEM- EDX and BET from spent catalytic cracking residues

The SEM of RCC images and the EDX spectrum of the RCC are shown in Fig. 3 and Fig. 4. The SEM provides a complete overview of the structural morphology of RCC before activation and after activation. The SEM images of RCC revealing the different size of particles with irregular shape. The activated RCC shown the clearer constituent elements of RCC. The RCC heating at 700–900 °C causes the loss of hydrocarbon impurities covered their surface. Therefore, reactivation of the RCC is needed to recover the surface areas and pores [20] and increasing the ratio of silica and alumina in the RCC as shown in Fig. 4.

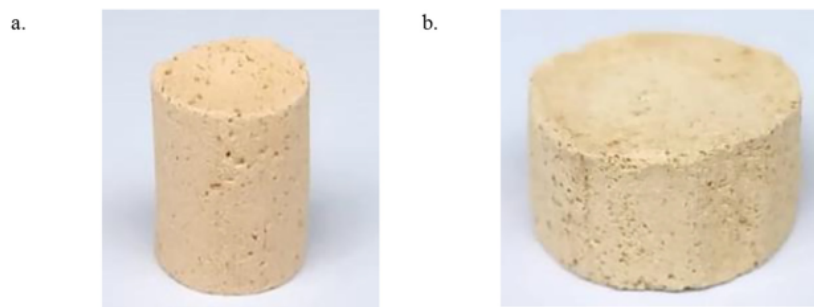


Fig. 1. Dimensional shape of ceramic adsorbent (a) diameter 10 mm, thickness 10 mm (b) diameter 20 mm, thickness 10 mm.

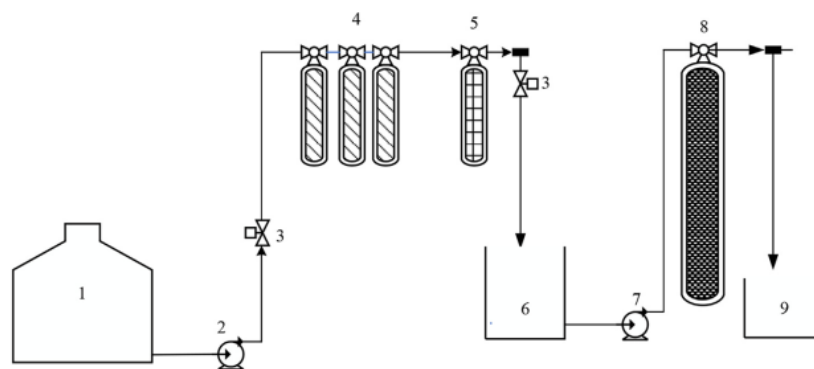


Fig. 2. Schematic of produced water treatment using ceramic adsorbents integrated with reverse osmosis (RO) (1. Feed tank 2. Centrifugal pumps 3. Valve 4. Propylene sediment filter 5. Adsorption column 6. Filtrate tank 7. RO Pump 8. RO membrane 9. Permeate tank).

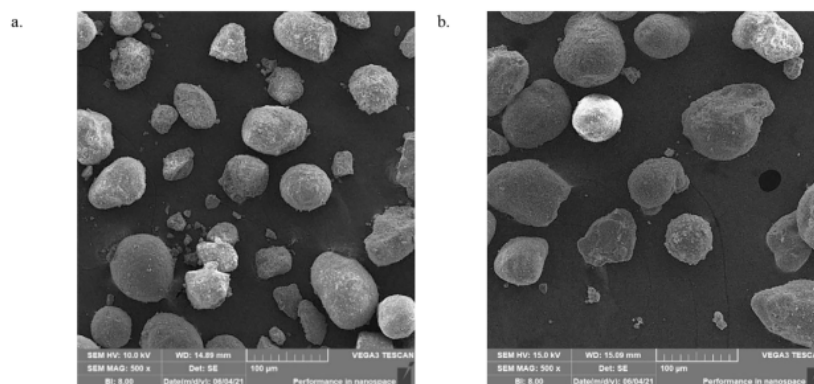


Fig. 3. SEM of RCC image at a magnification of 500 × (a) before activation (b) after activation.

Fig. 4 shows the EDX spectrum of RCC before activation and after activation. The peak of EDX spectra shown that silicon and alumina were the main elements of the RCC. It can be seen that there is an increase in the ratio of silica/alumina before and after activation. The silica/alumina ratio of RCC before activation was 1.26 and increased to 2.26 after activation. Increasing the silica and alumina content in the RCC can increase surface area and pore volume thus increases the adsorption capacity [21]. Ceramic adsorbent is composed of clay and RCC which is primarily contains silica and alumina. The presence of silicon dioxide (SiO<sub>2</sub>) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) in natural clay can increase the adsorption rate [20]. Most of the clays can swell and increase the space between their

layers to accommodate the adsorbed water and ionic species. Negatively charged alumina silicate in clay can adsorb water including heavy metals between it layers [22–23].

Brunauer Emmett Teller's (BET) analysis showed the RCC's surface area, pore size, and pore volume. The BET value of RCC is illustrated in Table 1. Based on BET Analysis, the surface area of the RCC is 62.00 m<sup>2</sup>/g, and the pore size is 1.6 nm. Based on the pore size, RCC is classified into micropores (diameter < 2 nm) [24–26]. The surface area of adsorbent is associated with their adsorption capacities.

Table 2 illustrated the BET of ceramic adsorbent A. The composition of ceramic adsorbent (70% clay and 30% RCC) is predomi-



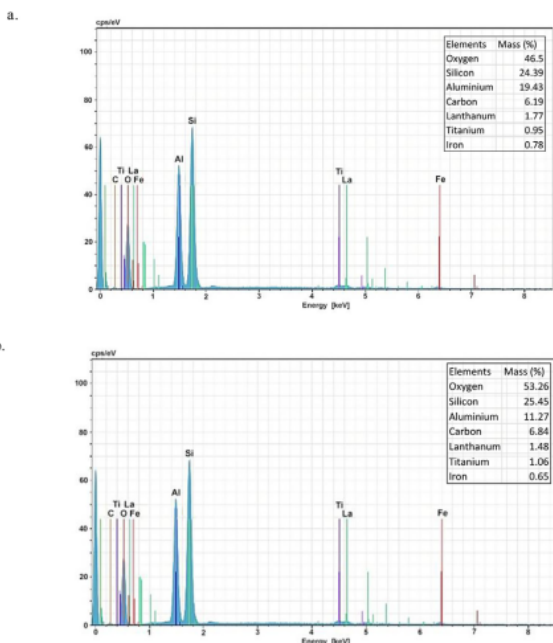


Fig. 4. EDX of the spent catalyst RCC spectra (a) before activation (b) after activation.

Table 1  
BET of RCC spent catalysts.

Characterization	Value
Specific surface area (m <sup>2</sup> /g)	62.00
Pore size (nm)	1.69
Pore Volume (cm <sup>3</sup> /g)	0.10

Table 2  
BET of Ceramic Adsorbent A (composition of 70% clay and 30% RCC).

Characterization	Value
Specific surface area (m <sup>2</sup> /g)	14.67
Pore size (nm)	2.93
Pore Volume (cm <sup>3</sup> /g)	0.03

antly **1** clay. The BET results are similar to the previous research using the ceramic filter with composition of 37.5% activated RCC, 60% clay and 2.5% of *Dioscorea hispida* starch [15]. As it can be seen, the surface area of ceramic adsorbent is lower than RCC spent catalyst but the pores size is larger than RCC. It is suggested that pore size of ceramic adsorbent is influence by the amount of clay. The pore size of ceramic adsorbent can be categorized as mesopores (pore diameter between 2 and 50 nm). As expected, the adsorption capacity of ceramic adsorbent will increase with increases the amount of clay in its composition.

### 3.2. Removal of TDS using ceramic adsorbent and integrated ceramic adsorbent and RO

The adsorption process is a phenomenon of separation on the surface due to the interaction between adsorbent and adsorbate. Adsorption can be grouped into physical and chemical adsorption depending on the surface properties of a material. A promising adsorbent must have an excellent affinity to adsorb compounds in the water and wastewater and low cost [25]. Physical adsorption is a separation process controlled by a weak inter molecule force between adsorbate and adsorbent. On the other hand **1** there is a good electron displacement in chemical adsorption due to the chemical bond between adsorbate and adsorbent surface [26].

Figs. 5 and 6 show the TDS removal of produced water using ceramic adsorbents integrated with RO membranes. The produced water sample is known to have a TDS value of 14,556 mg/L. Figs. 5 and 6 show that all types of adsorbents can decrease the TDS values in PW.

Fig. 5 show the best TDS removal is found by using ceramic adsorbent A with a composition of 70% clay and 30% RCC with an adsorbent diameter of 10 mm. It can be seen that TDS removal by ceramic adsorbent A is 74.58 % at contact time 60 min, and the flow rate 8 L/min. While ceramic adsorbent B reduce the TDS to 56.68% at a flow rate of 6L /min at **1** contact time 60 min. Adsorbent C reduces the TDS by 59.12% at a flow rate of 7 L /min and 60 min. Finally, adsorbent D decreased the TDS by 54.45% at a flow rate of 7 L / min and 60 min. As it can be seen, contact time and flow rate have a strong correlation with removal of TDS. However, the clay content in ceramic adsorbent has great influence on TDS adsorption. The decrease in TDS of produced water using ceramic adsorbents was influenced by pore distribution in adsorbents and ceramic adsorbents physical properties such as surface area and pore size. In addition, TDS adsorption by the adsorbent surface occurs due to the presence of hydrogen water bonds [27].

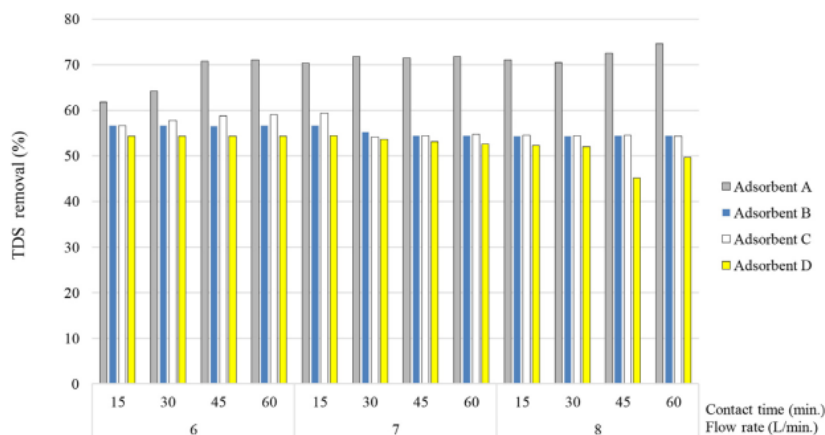


Fig. 5. Effect of contact time and flow rate on TDS removal by ceramic adsorbent.

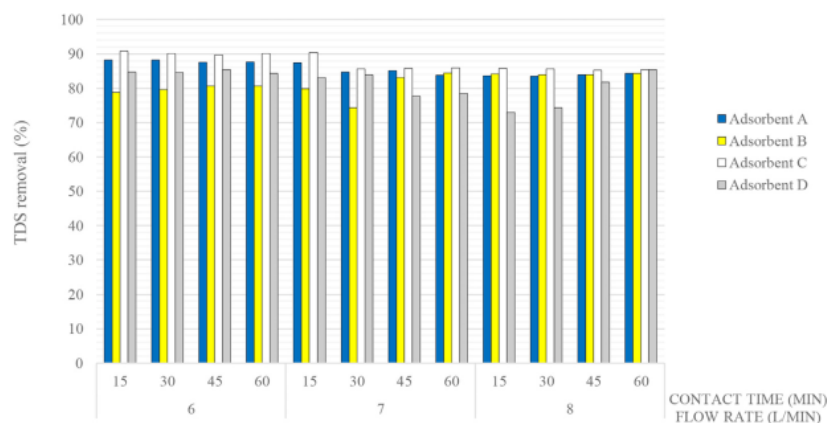


Fig. 6. Effect of contact time and flowrate on TDS removal by integrated of ceramic adsorbent and RO.

**Table 3**  
Optimum removal of TDS by ceramic adsorbents and integrated ceramic adsorbent-RO.

Ceramic adsorbent type	removal (%)	
	Ceramic adsorbent	Ceramic Adsorbent - Reverse Osmosis
A	74.58	88.18
B	56.68	84.41
C	59.40	90.73
D	54.45	85.44

Fig. 6 shows TDS removal in PW for using integrated ceramic adsorbent and RO. The low TDS adsorption is around 78.50% at 60 min of contact time and at a flow rate of 8 L/min by using ceramic adsorbent D and RO. In the current study the use of integrated ceramic adsorbent and RO (ceramic adsorbent-RO) effectively reduce the TDS from PW above 70%. The results showed that the ceramic adsorbent C integrated with RO effectively increase the TDS removal by 90.04% after 1 h contact time. The removal of TDS of ceramic adsorbent A-RO, ceramic adsorbent D-RO, and ceramic adsorbent B-RO decreased TDS from PW by 88.18%, 85.44%, and 84.41%, respectively. For comparison, the TDS removal by cera-

mic adsorbent and integrated ceramic adsorbent with RO is illustrated in Table 3.

Fig. 7 depict the TDS removal obtained for each type of ceramic adsorbent and the integrated ceramic adsorbent and RO membrane. It seen that TDS removal using ceramic adsorbent are ranges from 45.1% to 74.6%, while the TDS removal using an integrated ceramic adsorbent-RO membrane are between 73.0 % and 90.7%. The results showed ceramic adsorbent C-RO, ceramic adsorbent A-RO, ceramic adsorbent D-RO, and ceramic adsorbent B-RO decreased the TDS values by 1350 mg/L, 1720 mg/L, 2120 mg/L, and 2270 mg/L, respectively. The lowest TDS (1350 mg/L) content was found by using ceramic adsorbent C. In term of TDS, RO permeate met the standard of wastewater exploration of oil and gas because the TDS values are below 4000 mg/L.

#### 4. Conclusions

The following conclusion can be derived from the study.

- Spent catalysts of catalytic cracking residues and natural clay mixture can be used as ceramic adsorbents at certain composition effectively decrease the pollutants in produced water, especially the TDS value.

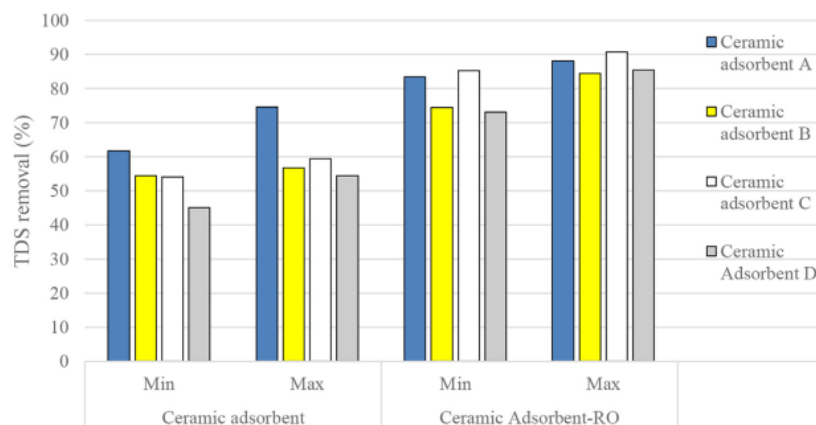


Fig. 7. Effect of ceramic adsorbent and integrated ceramic adsorbent-RO on TDS removal.

- Optimum TDS removal is 74.58% obtained by ceramic adsorbent A with 70% RCC, 30% clays, 10 mm adsorbent diameter at contact time 45 min, and a flow rate of 8 L/min. Optimum TDS removal by integrated ceramic adsorbent and RO is 90.73% obtained by using adsorbent C with 70 % RCC, 30% clay, and 10 mm adsorbent diameter.
- The removal efficiency of TDS in PW is in descending order, namely ceramic adsorbent A > ceramic adsorbent C > ceramic adsorbent B > ceramic adsorbent D.
- The removal efficiency of TDS in PW using integrated ceramic adsorbent and RO in descending order, namely ceramic adsorbent C > ceramic adsorbent A > ceramic adsorbent D > ceramic adsorbent B.
- Permeates obtained from integrated ceramic adsorbents with RO membrane meets oil and gas wastewater standards.

#### CRedit authorship contribution statement

**Netty Herawati:** Data curation, Investigation. **Muhammad Hatta Dahlan:** . **Maulana Yusuf:** Investigation. **Maulid M. Iqbal:** Methodology. **Kiagus Ahmad Roni:** Supervision. **Subriyer Nasir:** Conceptualization, Supervision.

#### 5 Data availability

Data will be made available on request.

#### Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Subriyer Nasir reports financial support was provided by Sriwijaya University.

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#### References

- [1] C. Zhang, W. Zhang, Y. Huang, X. Gao, Analysing the correlations of long-term seasonal water quality parameters, suspended solids and total dissolved solids in a shallow reservoir with meteorological factors, *Environ. Sci. Pollut. Res.* 24 (7) (2017) 6746–6756.
- [2] C. J. Cañedo-Argüelles, M., Kefford, B. J., Piscart, C., Prat, N., Schäfer, R. B., & Schulz, "Salinisation of rivers: an urgent ecological issue," *Environ. Pollut.*, no. 173, pp. 157–167, 2013
- [3] M. Brix, K. V., Gerdes, R., Curry, N., Kasper, A., & Grosell, "The effects of total dissolved solids on egg fertilization and water hardening in two salmonids—Arctic Grayling (*Thymallus arcticus*) and Dolly Varden (*Salvelinus malma*). *Aquatic toxicology*," vol. 92, no. 2, pp. 109–115, 2010
- [4] L. K. Weber-Scannell, P. K., & Duffy, "Effects of total dissolved solids on aquatic organism: a review of literature and recommendation for salmonid species," *Am. J. Environ. Sci.*, 2007
- [5] M. Said, D. Bahrain, R.F. Fitria, Treatment of produce water with a combination of electrocoagulation with iron (Fe) electrodes and adsorption using silica and activated carbon, *Int. J. Adv. Sci. Eng. Technol.* 11 (1) (2021) 204–212.
- [6] Pertamina (Persero) Refinery, "Sustainability Report. Tech. Rep. Palembang: PT Pertamina (Persero) Refinery Unit III Plaju," 2017, pp. 1–148
- [7] S. Munirasu, M.A. Haija, F. Banat, Use of membrane technology for oil field and refinery produced water treatment - a review, *Process Saf. Environ. Prot.* 100 (2016) 183–202.
- [8] M. A. Al-Ghouti, M. A. Al-Kaabi, M. Y. Ashfaq, and D. A. Da'na, "Produced water characteristics, treatment and reuse: A review," *J. Water Process Eng.*, vol. 28, no. September 2018, pp. 222–239, 2019.
- [9] M. A. Al-Kaabi, M. A. Al-Ghouti, M. Y. M. Ashfaq, T. Ahmed, and N. Zouari, "An integrated approach for produced water treatment using microemulsions modified activated carbon," *Journal of Water Process Engineering*, vol. 31, 2019.
- [10] S. Jiménez, M. Andreozzi, M.M. Micó, M.G. Álvarez, S. Contreras, Produced water treatment by advanced oxidation processes, *Sci. Total Environ.* 666 (2019) 12–21.
- [11] T. S. Alomar, B. H. Hameed, M. Usman, F. A. Almomani, M. M. Ba-Abbad, and M. Khraisheh, "Recent advances on the treatment of oil fields produced water by adsorption and advanced oxidation processes," *J. Water Process Eng.*, vol. 49, no. July, p. 103034, 2022
- [12] P.X. Pinto, S.R. Al-Abed, D.A. Balz, B.A. Butler, R.B. Landy, S.J. Smith, Ein Review über Behandlungstechnologien im Labor- und Pilotmaßstab zur Minderung der Mineralisation aus Abwässern des Kohlebergbaus, *Mine Water Environ.* 35 (1) (2016) 94–112.
- [13] J. Peng, K. Kumar, M. Gross, T. Kunez, Z. Wen, Removal of total dissolved solids from wastewater using a revolving algal biofilm reactor, *Water Environ. Res.* 92 (5) (2020) 766–778.
- [14] S. Saja et al., Fabrication of low-cost ceramic ultrafiltration membrane made from bentonite clay and its application for soluble dyes removal, *J. Eur. Ceram. Soc.* 40 (6) (Jun. 2020) 2453–2462.
- [15] R.E.D. Putri, S. Nasir, F. Hadiah, Application of ceramic filter and reverse osmosis membrane for produced water treatment, *Pollution* 8 (4) (2022) 1103–1115.
- [16] Z. Zhang et al., Mesoporous polymer-derived ceramic membranes for water purification via a self-sacrificed template, *ACS Omega* 5 (19) (2020) 11100–11105.
- [17] A. Abdullayev, M. F. Bekheet, D. A. H. Hanaor, and A. Gurlo, "Materials and applications for low-cost ceramic membranes," *Membranes*, vol. 9, no. 9. MDPI AG, 2019
- [18] P. K. B. Herbudiman, A. Setyaning, "The Use Of Spent Catalyst RCC-15 As Powder On Environmental- Friendly High-Performance Self- Compacting Concrete," pp. 89–94, 2011.
- [19] B. B. Mubiyai, M. P., Muleja, A.M. and Mamba, "Data on physicochemical properties of natural clay and natural clay/multiwalled carbon nanotubes composite materials for various applications possibilities," *Data Br.*, no. 39, p. 107682, 2021
- [20] G. Lu, X. Lu, P. Liu, Reactivation of spent FCC catalyst by mixed acid leaching for efficient catalytic cracking, *J. Ind. Eng. Chem.* 92 (Dec. 2020) 236–242.
- [21] N. K. Erliyanti, S. Muljani, D. Baskoro, and N. W. Erza Prastika, "Synthesis and Characterization of Adsorbent from Solid Waste of Ceramics Industry," *J. Phys. Conf. Ser.*, vol. 1569, no. 3, 2020.
- [22] A. Amari, H. Gannouni, M. I. Khan, M. K. Almesfer, A. M. Elkhaleefa, and A. Gannouni, "Effect of structure and chemical activation on the adsorption properties of green clay minerals for the removal of cationic dye," *Appl. Sci.*, vol. 8, no. 11, p. DOI: 10. 3390/app8112302., 2018.
- [23] M.K. Uddin, A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade, *Chem. Eng. J.* 308 (2017) 438–462, <https://doi.org/10.1016/j.cej.2016.09.029>.
- [24] D. V Ngoc Dung, T. T., Phan Thi, L. A., Nam, V. N., Nhan, T. T. and Quang, "Preparation of silver nanoparticle-containing ceramic filter by in-situ reduction and application for water disinfection," *J. Environ. Chem. Eng.*, no. 7 (3), p. 103176, 2019
- [25] E. Annan, E., Agyei-Tuffour, B., Bensah, Y. D., Konadu, D. S., Yaya, A., Onwona-Agyeman, B. and Nyankson, "Application of clay ceramics and nanotechnology in water treatment: A review," *Cogent Eng.*, no. 5 (1), pp. 1–35, 2018
- [26] H. Quallal, Kinetic, isotherm and mechanism investigations of the removal of phenols from water by raw and calcined clays, *Heliyon* 5 (5) (2019) 01616.
- [27] E. Jang, E., Jeong, S. and Chung, "Application of three different water treatment technologies to shale gas produced water," *Geosystem Eng.*, no. 2 (20), pp. 104–110, 2017

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