Utilization of supercritical carbon dioxide (SC-CO$_2$) in lipids extraction from sewage sludge cake: A preliminary study

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Abstract. Sewage sludge containing a large number of lipids that can be recovered and utilised as a promising raw material in the production of biodiesel. Studies have been conducted to extract lipids from sludge using conventional solvent methods. However, all these conventional methods have some limitations such as extensive product separation and long extraction time (between 4 to 8 hours), which lead to high energy consumption. Supercritical carbon dioxide extraction (SFE) which utilises carbon dioxide (CO$_2$) gas at its critical condition as solvent has been studied extensively in various fields for oil extraction especially for plant and vegetative. This is due to the shorter extraction time and the lipids can be easily separated from the extraction system. The present research has undertaken a comparison study of supercritical carbon dioxide (SC-CO$_2$) utilisation in the extraction of lipids from sewage sludge against conventional soxhlet extraction of methanol and ethanol as solvent. The extraction of lipids from sewage sludge utilising SC-CO$_2$ extraction was successfully being conducted with lipids yield of 0.69 % within 0.5 hours at the operating temperature of 50 °C and pressure of 20 MPa. The lipids were easily separated subsequently from the SFE system when CO$_2$ is being released in gas form through the outlet valve during lipids collection. Whilst soxhlet extraction using methanol and ethanol as solvent (sludge: solvent ratio of 1:10) managed to extract 1.95 % and 2.81 % within 4 hours of extraction time at 60 °C, with the additional time needed to separate the lipids from solvent by evaporation.
1. Introduction
Municipal wastewater treatments plants generate a massive amount of sewage sludge each year as residual from wastewater treatment originated from household and light industrial sectors. The generation of annual sewage sludge per capita is estimated within the range of 0.1 to 30.8 kg/population.year [1–3]. Massive economic development and the population increase led to rapid urbanization resulting in the generation of a huge volume of sewage sludge, which posing significant environmental challenges for management and disposal. Many countries regulate the usage of sludge for land application such as fertilizer due to poor odour and the presence of heavy metals, toxic organic compounds, and pathogenic microorganism, while sludge incineration produces emissions comprising heavy metals and dioxins [4, 7]. Sewage sludge comprises a lipids fraction, which is a composite organic matrix containing oils, greases, fats and long-chain fatty acid originated from domestic and industrial wastes [4]. The volume of sewage sludge could be reduced by extracting the lipids fraction and converting it into a value-added product as a viable alternative in sustainable sludge management and disposal [5–9].

Lipids are extracted from sewage sludge mostly using solvent extraction (solid-liquid extraction) by organic solvents (non-polar or polar solvent) or supercritical carbon dioxide (SC-CO₂) [4, 5, 10]. The lipids extraction and its yield are influenced by the type of solvent used due to its unique characteristics and also the extraction parameters such as temperature, extraction time and the sludge-to-solvent ratio [10, 11].

The extraction of lipids using SC-CO₂ is a sustainable alternative compared to other solvents because carbon dioxide (CO₂) is inexpensive, readily available, non-toxic, and non-flammable [12]. SC-CO₂ utilize its solvating properties when the temperature and pressure are raised beyond the critical point which are 30.9 °C and 7.39 MPa [14, 16]. The SC-CO₂ has desirable properties such as high diffusivity, low surface tension and viscosity, density, heat capacity, thermal conductivity and ease of high solute recovery, which make it suitable for challenging extraction processes [5, 12, 13]. Supercritical fluid extraction technology with supercritical carbon dioxide (SFE-CO₂) is an effective extraction and sterilization technology and SC-CO₂ is an excellent solvent for the extraction of thermally sensitive compounds and materials [14, 15]. The SC-CO₂ technology has been proven as promising, advantageous and environmentally friendly over other conventional methods for extraction and fractionation of oil and its valuable components especially for plant and vegetative [14, 17]. Unfortunately, limited study has been conducted on the extraction of lipids from sewage sludge by using SC-CO₂. Therefore, this study aims to compare the lipids extraction from sewage sludge cake utilizing SC-CO₂, methanol, and ethanol as solvent.

2. Material and method

2.1. Sludge sample collection, preparation, and characterization
The sewage sludge cake was gathered from sludge storage yard using a shovel at 5 different points with similar weight. The sludge cake was well mixed to ensure the sample is consistent. The sludge cake was kept in a zipper bag and transported in a cool box to the laboratory.

Upon reaching the laboratory, the sludge cake was analyzed for moisture content (MC), volatile matter, crude ash, fixed carbon and elemental composition. Heavy metal analysis was also conducted for iron (Fe), copper (Cu), zinc (Zn) and lead (Pb).

The remaining sludge cake was kept in the refrigerator at 4 °C until further processing and testing. The sludge cake was oven-dried at temperature 105 °C to obtain <5 % MC. Then, the dried sample was ground using pastel & mortar and sieved through a 100 mesh before lipids extraction [18].

2.2. Lipids extraction experiments
Two extraction processes used for this study: Supercritical fluid extraction (SFE) using SC-CO₂ and soxhlet extraction using methanol and ethanol as the solvent. All the chemicals used were of analytical grade and were stored in a dry cabinet to avoid any changes due to humidity.
2.2.1. Extraction by SC-CO$_2$. Lipids extraction by the SC-CO$_2$ extraction system was conducted in static mode. Briefly, the desired amount of sludge sample was placed inside the high-pressure extractor vessel and the heating system is switched on. Carbon dioxide was pumped into the vessel at the desired temperature until the pressure reaches its operating value. The sludge sample was left in contact with the CO$_2$ fluid for the intended extraction time. After extraction, the outlet valve was opened slowly to collect the extracted lipids.

2.2.2. Extraction by soxhlet extractor using solvent. Lipids extraction by Soxhlet extractor was conducted using two different solvents: methanol and ethanol. The sludge sample was placed in a thimble and put into the extraction chamber. The solvent was filled up into the round bottom flask and placed on the heating mantle. All parts (round bottom flask, extraction chamber and condenser) were assembled accordingly and the extraction process was started at the desired temperature and extraction time. After extraction, the resultant mixture was filtered and further concentrated using a rotary evaporator at a temperature of 80 °C and under vacuum (50 mbar). The resultant lipids were stored in a desiccator and weighed the day after.

2.2.3. Lipids yield. The extracted lipids yield by both extraction methods was calculated using the following equation [19].

\[
\text{Lipid Yield} \% = \left( \frac{\text{Residual mass} \ [g]}{\text{Sludge solid mass} \ [g]} \right) \times 100\% \quad (1)
\]

3. Results and discussion

3.1. The site and sample collection
The sewage sludge was collected from the sludge storage yard of the Centralized Sludge Treatment Facility (CSTF), situated in Central Malacca District, Malacca, Malaysia. The facility is being managed and operates by the Indah Water Konsortium Sdn. Bhd (IWK Malacca), where it is designed to cater 190 m$^3$/day of wastewater or 300,000 population equivalents [20]. The facility received an average of 63.86 m$^3$/day of wet sludge to be treated and produced an average of 1.2 ton/day of sludge cake by centrifuge dewatering unit [20].

Figure 1 shows the flow of the sludge treatment process within the CSTF [20]. The sewage sludge generated from individual septic tanks (IST), sewage treatment plants (STP) and communal septic tanks (CST) is transported by a tanker. Upon reaching the facility, the sludge is passed through a coarse screen into a scum collection tank to remove oil and grease. The screened sludge is temporarily stored in a sludge holding tank. The sludge is mixed with a polymer for thickening and subsequently dewatered by centrifugation to ensure the sludge is at least 20 % dried. The dewatered sludge as sludge cake is transported using sludge hoppers to the sludge cake storage yard (figure 2) and keep until disposal.
3.2. Characteristics of the sludge cake

Preliminary analysis (physical and chemical analysis) was conducted on the sludge cake obtained from the CSTF. Properties of the sludge cake such as moisture content, elemental analysis, ash content, volatile matters and fixed carbon are shown in Table 1.

The collected sludge sample from CSTF had an initial moisture content of 66.68 wt. % and reduced subsequently to 2.36 wt. % following oven drying for 6 hours at 105 °C as shown in Figure 3. Oven drying at 105 °C shows the highest extracted lipids compared to other drying methods such as the...
addition of MgSO₄·H₂O, freeze-drying, fume hood-drying and sun-drying [7]. The final moisture content of the sludge is a significant factor affecting the extraction of lipids because water can surround the sludge particles and hinder efficient solvent penetration into the sludge [7]. The sewage sludge also had high volatile matter (35.98 %) and fixed carbon (55.60 %) and low ash content (0.85 %). Heavy metal analysis conducted shows high Fe content, followed by Zn, Cu and Pb.

Table 1. Characteristics of sewage sludge cake.

| Properties       | Item                      | Value                      |
|------------------|---------------------------|----------------------------|
| Moisture content | Sludge Cake               | 66.68 ± 1.67 %             |
|                  | Oven dried sludge (105 °C, 6 hr) | 2.36 ± 0.34 %             |
| Elemental Analysis | Carbon                   | 0.26 ± 0.07 %             |
|                  | Hydrogen                  | 0.9 ± 0.00 %              |
|                  | Oxygen                    | 4.63 ± 0.02 %             |
| Ash Content      |                           | 0.85 ± 0.06 %             |
| Volatile Matters |                           | 35.98 ± 7.95 %            |
| Fixed Carbon     |                           | 55.60 ± 7.89 %            |
| Heavy metal      | Fe                        | 141.28 ± 12.69 mg/L       |
|                  | Cu                        | 5.03 ± 0.88 mg/L          |
|                  | Zn                        | 30.95 ± 1.63 mg/L         |
|                  | Pb                        | 0.81 ± 0.06 mg/L          |

Figure 3. Moisture content for oven-dried sludge.
3.3. Sludge particle size distribution after oven drying.
Particle size analysis was conducted on the oven-dried sludge sample used in the SC-CO$_2$ and soxhlet extraction. Figure 4 shows the largest fraction of size lies in range $0.425 \leq x < 2$ mm, followed by $<0.425$ mm, $2$ mm $\leq x <3.35$ mm and $x \geq 3.35$ mm.

![Figure 4. Particle size range for sludge sample.](image)

3.4. Lipids yield for SC-CO$_2$ and soxhlet extraction.
Figure 5a shows the lipids collection from the outlet valve after extraction by SC-CO$_2$. A batch SC-CO$_2$ extraction process was conducted under the constant operating parameter of 20 MPa of pressure and 50 °C of temperature for 0.5 hour and yielded 0.65 % of lipids. The recovered lipids were high in viscosity and yellowish in appearance as shown in figure 5b and figure 5c.

![Figure 5. Lipids collection activity after SFE-CO$_2$ extraction.](image)
Figures 6 and 7 show the lipids yield from soxhlet extraction by methanol and ethanol as solvent (sludge: solvent ratio of 1:10). The yield of lipids significantly increased ($R^2 > 0.9$) with the increased extraction time (4, 5 and 6 hours) for both solvents. The extraction temperature of 80 °C gives the highest lipids yield for both solvents. The extraction using ethanol yielded more lipids at all temperature (60, 70 and 80 °C) and extraction time (4, 5 and 6 hours) with the highest lipids yield (5.16 %) compared to methanol (4.05 %).

Extraction of lipids by SC-CO$_2$ yielded the lowest lipids followed by methanol and ethanol (SC-CO$_2$ < methanol < ethanol). It is because the SC-CO$_2$ has a lower polarity index compared to ethanol and methanol [5, 21, 22]. Even though the lipids extracted from SC-CO$_2$ is lower compared to soxhlet extraction, a shorter extraction time (0.5 hour) needed for this process. Furthermore, lipids were immediately separated from the CO$_2$ and no residual traces of solvent once CO$_2$ becomes gaseous after being released from the SC-CO$_2$ system due to depressurization [14, 16].

![Figure 6. Lipids yield for extraction using soxhlet extraction and methanol as solvent.](image-url)
4. Conclusion
The extraction of lipids from sewage sludge utilizing SC-CO$_2$ extraction was successfully being conducted with lipids yield of 0.69 % within 0.5 hours at the operating temperature and pressure of 50 °C and 20 MPa. Lipids were easily separated subsequently from the SC-CO$_2$ system when CO$_2$ is being released in gas form through the outlet valve during lipids collection. Whilst soxhlet extraction using methanol and ethanol as solvent (sludge: solvent ratio of 1:10) managed to extract 1.95 % and 2.81 % within 4 hours of extraction time at 60 °C, with the additional time needed to separate the lipids from solvent by evaporation.

Limitation on the usage of SFE-CO$_2$ in the industrial process is always associated with low lipids yield, high initial investment costs as a stand-alone technology and the end-product, which is not at of high-value which hinder the further development of this technology especially in lipids extraction from sewage sludge. Hence, further exploration is needed to be conducted in SC-CO$_2$ lipids extraction from sewage sludge specially to increase the lipids yield such as the variation of SC-CO$_2$ techniques (static, dynamic and combination mode), co-solvent usage and optimization of extraction parameters (temperature, pressure, extraction time and CO$_2$ flow rate) and the quality to be used for the high-value product. Techno-economic and life cycle assessment of SFE-CO$_2$ in this application also can be conducted as a whole scheme (wastewater treatment, sludge management and disposal, lipids extraction and end-product refinery) rather than a stand-alone technology to assess the sustainability of integrating SFE-CO$_2$ in the overall processes.

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Figure 7. Lipids yield for extraction using soxhlet extraction and ethanol as solvent.
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