



Communication Impact of Water Circularity on Climate Change: Removal of Fats, Oils and Grease (FOG) from Water Using Green and Simple Extraction Methods

Andrés S. Lagos ^{1,2} and Andrea C. Landázuri ^{1,3,4,5,*}

- ¹ Applied Circular Engineering & Simulation Group (GICAS), Chemical Engineering Department, Colegio de Ciencias e Ingenierías, Universidad San Francisco de Quito USFQ, Diego de Robles y Vía Interoceánica, Quito 170901, Ecuador
- ² Área de Ambiente y Sustentabilidad, Universidad Andina Simón Bolívar, Quito 170525, Ecuador
- ³ Institute for Energy and Materials, Universidad San Francisco de Quito USFQ, Diego de Robles y Vía Interoceánica, Quito 170901, Ecuador
- ⁴ Instituto de Investigaciones Biológicas y Ambientales (Biósfera), Universidad San Francisco de Quito USFQ, Diego de Robles y Vía Interoceánica, Quito 170901, Ecuador
- ⁵ Instituto IBioMed, Universidad San Francisco de Quito USFQ, Diego de Robles y Vía Interoceánica, Quito 170901, Ecuador
- * Correspondence: alandazuri@usfq.edu.ec

Abstract: Climate change is impacting the severity of water pollution, and polluted water bodies have an impact on climate change. Increased precipitation and atmospheric temperature changes affect the flow of water bodies, causing interactions in the chemical kinetics of the contaminants present in water that should not be present in the first place. Likewise, anthropogenic activities and their waste management require urgent actions for the mitigation and adaptation to climate change. Fats, oils and grease (FOG) present in water are difficult to remove and affect the drinking water or wastewater treatment trains; that is, FOG can aggregate and clog subsequent operations and are susceptible to temperature changes. Relevant advances in FOG removal using oleic acid as a model compound submitted to a liquid–liquid extraction under menthol:lactic acid deep eutectic solvent (DES) mixture is presented.

Keywords: water circularity; deep eutectic solvents; menthol; lactic acid; oleic acid; FOG; water treatment; climate change

1. Introduction

FOG are non-polar, hydrophobic chemical substances, and often toxic, organic (not to mention, expensive) solvents must be used for their dilution. During the removal of FOG from water, toxic by-products (e.g., acetate) may be left in the process, and these types of organic compounds have carcinogenic effects in animals, plants and humans [1]. For industries and Water Resource Recovery Facilities (WRRF), the presence of FOG impedes the optimal transport of fluids because these compounds adhere to pipe walls, causing obstructions and economic losses as a result of maintenance, in addition to the consequent environmental impact due to poor management of this waste [2].

FOG pollution comes from a variety of sources, including industry and the domestic use of edible oils. The largest source of pollution by fats is the production and extraction of palm oil, with high concentrations around 4000 to 6000 mg/L [1,3]. As for domestic use, a concentration between 50 and 100 mg/L [1,4] is reported, although kitchen waste is the most important contributor of oils in greywater discharges. Other sources of polluting oils and fats are found in industries that use them in their manufacturing processes, such as food (use of vegetable oils), metal and oil refining (use of oils of non-vegetable origin) [1]. These forms of pollution, through the addition of toxic chemicals and/or man-made by-products,



Citation: Lagos, A.S.; Landázuri, A.C. Impact of Water Circularity on Climate Change: Removal of Fats, Oils and Grease (FOG) from Water Using Green and Simple Extraction Methods. *Sustainability* **2023**, *15*, 4176. https://doi.org/10.3390/su15054176

Academic Editors: Brian Vejrum Wæhrens, Rodrigo Salvador, Peder Veng Søberg and Samuel Brüning Larsen

Received: 2 November 2022 Revised: 26 January 2023 Accepted: 15 February 2023 Published: 25 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). can generate some toxic and greenhouse gases, which can subsequently contribute to global warming or further environmental threats [5,6]; for instance, solutions for the removal of FOG that allow water to reenter productive processes (herein the term "water circularity") and water resource facilities or drinking water plants need to be found.

Deep eutectic solvents (DES) [7] have been investigated to exploit their uses for organic matter extraction, inorganic ion extraction, extractive distillation, gas absorption and liquid– liquid extraction [8]. Despite the fact that the solubility capacity of long hydrocarbon chains in a DES matrix has already been studied, the application of DES for FOG removal from water from a remediation perspective requires more exploration, especially in the oil and gas sector [9], oil spill removal [10] and wastewater and household management. Estimates for household and industrial oil run off vary greatly because these are difficult to measure [11]. In developing countries such as Ecuador, greywater is often disposed of directly into water bodies, although some interception solutions of these waters are being provided by Ecuadorian water companies, and this type of technology has not yet been applied. In addition, Ecuador shelters the Galápagos Islands, which is a unique environmental area on the planet, and therefore practical and sustainable solutions are needed. DES-like mixtures are tunable solvents that can be customized for a particular type of chemistry application, are easy to handle and are available from relatively inexpensive components; the production of DES involves the simple mixing of two components, generally with moderate heating and stirring, lowering the cost of production compared to conventional solvents and allowing large-scale applications [12]. DES show low vapor pressure, are non-flammable and contain large and asymmetric ions that have low lattice energy and therefore low melting points; this specific temperature is also known as "eutectic point" [12,13]. Because this temperature is observed at the specific molar fraction of one of the components of the mixture, new terms have been suggested to name these mixtures, such as Low-Transition Temperature Mixture (LTTM), which shows a glass transition temperature lower than the melting points of the pure components [14]. Nevertheless, given that these substances are commonly referred to as DES by other authors, including Andrew Abbott, a pioneer in the research of these solvents, throughout this work we will also call these mixtures DES, despite the different molar ratios where the eutectic point is reached [7,15,16].

This work presents, for the first time, the removal results of oleic acid as a model compound of FOG during an extraction process involving a 1:1 equimolar mixture of menthol and lactic acid. These results are part of a green bioremediation technology that is currently being developed that is aimed at circular water management and contributes to lowering carbon emissions based on FOG extraction via Deep Eutectic Solvents to partially substitute current FOG removal practices.

2. Materials and Methods

All reagents used in DES synthesis were of analytical grade. DL-Menthol, USP grade, was purchased from La Casa de los Químicos S.A. (Ecuador). Extra pure grade (>90%) lactic acid was purchased from TM Media and oleic acid (ACS > 99%) from Fisher Scientific (Waltham, MA, USA). For FOG analysis, chloroform (ACS > 99%) was purchased from Sigma Aldrich—Supelco (Sofia, Bulgaria). Throughout all the experimental runs, deionized water (ASTM type II) was used.

Different factors were studied in this work. Here we present the most typical conditions for FOG removal in water. A 1:1 equimolar mixture of menthol:lactic acid is produced by weighing 156.27 g (1 mol) of menthol and 90.03 g (1 mol) of lactic acid. This mixture is stirred at 500 rpm and heated at 40 °C for one hour. The resulting mixture is clear, and it is transferred to an amber container for storage and kept in a cool and dry place, without exposure to light. Artificial water with oleic acid (600 mg/L) is prepared. The solvent is added and stirred at 500 rpm for 15 min. The aqueous and organic phases are allowed to separate for mass transport to take place. This separation time will be no less than eight hours. Subsequently, the aqueous phase is decanted, which will be an almost free-of-fatty acids phase. The supernatant can be collected and reused for more extractions, never exceeding five reuse cycles.

DESs were characterized by Fourier Transform Infrared (FTIR) spectrophotometry to analyze the hydrogen bonds present in the eutectic mixture. A spectrophotometer (Agilent Cary 630) with an ATR module was used to record all spectra within the 4000 to 600 cm⁻¹ range. Origin Pro and data processing software (OriginLab Corporation, Northampton, MA, USA) was used to analyze the peaks obtained in the FTIR spectra.

The EPA 1664B method was used with the modification of the use of chloroform as an extraction solvent as an alternative to hexane. Results were validated using the original gravimetric method EPA 1664B ("Method 1664, Revision B: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel-treated n-Hexane Extractable Material (SGT-HEM; Non-Polar Material) by Extraction and Gravimetry", 2010). The repeatability of the analyzes carried out with chloroform was validated, as well as the repeatability analysis of the extraction of oils and fats using n-hexane, according to the standards required by the EPA 1664B method.

The influence of the variation on stirring speeds, contact time and phase separation time was also evaluated.

3. Results and Discussion

Figure 1 shows the spectra of the infrared region for the DES, made up of the equimolar mixture of menthol:lactic acid (1:1 ratio), as well as its pure components. These spectra contain important information regarding the bonds of the compounds involved, especially information relating to the hydrogen bonds formed between them. Indeed, stretching vibrations of the bonds in the region between 3500 and 3100 cm⁻¹, which correspond to the vibrations of the O–H bonds, are observed. A characteristic peak can be noted for menthol (hydrogen bond donor), with a maximum at 3237 cm⁻¹ due to the characteristic O–H bond of cyclohexanol. In the same way, a wide peak occurs at 3147 cm⁻¹ due to the vibrations of the O–H groups of lactic acid. In addition, the stretching vibrations of the O–H bond stretching band (3370 cm^{-1}), as well as characteristic peaks in the region of 3000–2800 cm⁻¹ typical of the hydrogen bonds formed between the hydroxyl groups of menthol and the hydroxyl and carboxyl groups of lactic acid [17–19], are also observed.

Figure 2 shows notable results of oleic acid (as a model fatty acid representing FOG) removal efficiency from water using the 1:1 DES mixture. It has been shown that mentholbased hydrophobic deep eutectic solvents can be used in wastewater remediation. In fact, there are some studies where DES can hatch pollutants by hydrogen bonds between organic pollutants and DES, as well as ionic interactions with heavy cations [19–21]. These interactions are stronger with the use of short-chain carboxylic acids and alcohols such as formic, acetic, and propionic acids, and n-butanol in deep eutectic mixtures with DL-menthol [22]. Highly efficient oleic acid removals (>91%) in water with an initial concentration, C_o , of 600 mg/L were obtained at specific stirring speeds, contact times and phase separation times.

Figure 2a shows FOG removal as a function of DES (1:1) to polluted water ratio with an initial concentration, C_0 , of 600 mg/L, 500 rpm during 15 min. It can be observed that as the DES to polluted water ratio is greater, removal efficiency is also better. It is hypothesized that because there is a greater amount of DES in the water to be treated, there is a greater possibility that undissolved fatty acids in the water will be transferred to the organic phase and will easily dissolve in the DES. This is compatible with liquid–liquid separations with substances more miscible in one phase than in another.

Figure 2b presents removal as a function of initial concentration, C_0 , at 500 rpm over 15 min where, by increasing the initial concentration of the pollutant (oleic acid), the removal efficiency each time is lower. Typical concentrations up to 1000 mg/L provide more than 80% pollutant removal. This is important because it can provide initial operating conditions in the case of scaling up the process to pilot plant and industrial levels.



Figure 1. FTIR spectra of the equimolar menthol:lactic acid eutectic mixture (1:1 ratio), and its pure components: lactic acid and menthol.

Figure 2c depicts the removal as a function of stirring contact time at 500 rpm and $C_o = 600 \text{ mg/L}$. The contact time during the agitation process is important as it determines how much of the pollutant in the water can be dissolved in the organic phase. By increasing the contact time, the efficiency of the process is always higher, reaching over 99% removal with a stirring time of 30 min. Typical conditions, for efficient removal processes, can take place for 15 min with considerable removal up to 90% for this pollutant model.

Removals as a function of stirring speed (Figure 2d) with $C_o = 600 \text{ mg/L}$ and 15 min contact time, shows interesting results, where high and low stirring speeds have a considerable influence on the process. Speeds lower than 300 rpm show less than 85% removal, while speeds higher than 1000 rpm can obtain the same removal percentage. For this reason, it is necessary to consider a moderate speed to obtain removals greater than 90%. This phenomenon may be due to the transport of the pollutant in the organic and aqueous phases. With a lower speed of agitation, it is not possible to mix both phases, and the transport of the contaminant is impoverished, while at high speeds of agitation, the flow becomes turbulent in the organic/aqueous interface, preventing a correct transport of the pollutant between both.

Removals as a function of phase separation time (Figure 2e) with 500 rpm and $C_o = 600 \text{ mg/L}$ and 15 min contact time reveals how necessary a correct phase separation time is. After the stirring time, the time in which the separation takes place is fundamental because in the interface of both organic and aqueous phases there is still the transport of contaminants. In addition, as a product of the emulsion obtained after stirring, if both phases are separated quickly, it is not possible for the emulsion to break, leaving part of the DES trapped in the aqueous phase, as well as water in the organic phase. Separation times of less than 4 h diminish removal to less than 75%, while times greater than 6 h increase removal to more than 87% [19,21]. To depict the potential application of the selected DES-like mixtures with other ratios, Figure 2f has been included. It can be observed that FOG removal can still be improved with other ratios.



Figure 2. FOG percent removals using oleic acid as the model compound of FOG. Sensitivity analyses of removal percentages as a function of: (**a**) DES (1:1) to polluted water ratio with an initial concentration, C_o , of 600 mg/L, 500 rpm over 15 min, (**b**) C_o at 500 rpm over 15 min, (**c**) stirring contact time at 500 rpm and $C_o = 600 \text{ mg/L}$, (**d**) stirring speed with $C_o = 600 \text{ mg/L}$ and 15 min contact time, and (**e**) phase separation time with 500 rpm and $C_o = 600 \text{ mg/L}$ and 15 min contact time; (**f**) shows that there are still other ratios of menthol:lactic acid to evaluate that may even enhance FOG removal.

After the extraction treatment, it is expected that there is no change in the chemical structure of the DES and that there is a greater number of linkages due to the solubility of fatty acids (oleic acid) in the organic phase [18,19,23]. This was corroborated and, as can be seen in Figure 3, there are no differences in the presence of peaks for the before (BT) and after (AT) treatments. The only difference is observed in the relative height of the peaks corresponding to the carboxylic groups, especially in the range of O–H bonds (3500–2800 cm⁻¹) and C=O bonds (1700 cm⁻¹), which are expected because the DES mixture is taking up more carboxylic groups (present in oleic acid) in the removal process, and the very small amount of water that is slightly soluble in DES.



Figure 3. FTIR spectra of the equimolar DES formed by menthol:lactic acid (1:1 ratio). Spectra are presented both before (DES 1:1 BT) and after (DES 1:1 AT) removal treatment.

These results bring the motivation to continue to pursue this investigation under more complex and realistic polluted water matrices polluted with FOG. Compared to traditional physical methods, it has been found in our study that comparable removal efficiencies are achieved (over 95% when optimizing the studied parameters). First, a study found that gravity separation and dissolved air flotation methods achieve efficiencies of 50-60%, while 90% removal can be achieved if surfactant additives are used. On the other hand, through chemical methods such as flocculation and electrochemical technologies, removals of up to 90% can be achieved. Finally, through demulsifying methods using carbon nanoparticles, oil removal efficiencies of up to 99% are achieved [24]. FOG is chemically characterized as a mixture of free long-chain saturated and unsaturated fatty acids and triacylglycerols such as palmitic, oleic, linoleic and stearic acids [25]. Palmitic and oleic acids, as well as stearic acid, have been used as FOG standards. Furthermore, the rheological aspects of these mixtures are currently being investigated, and it has been found that the DES mixtures under study show a Newtonian behavior when continuous shear test were developed; however, a viscoelastic response was observed during oscillatory shear tests at high frequencies [26]. This is crucial for the quantification of the pumping and energy requirements for scale-up purposes. It is also worth mentioning that this DES mixture can be reutilized for subsequent extractions.

4. Conclusions

This research work is the prelude of a potential partial "carbon neutral" solution for FOG removal during water resource recovery within an industrial and household scope that can lead to business opportunities and partnerships for its application at a larger scale, and replication worldwide, supported with technoeconomic reports that compare the proposed technology to classic and other green removal methods, such as those from agro-industrial wastes. It could also lead to the possible generation of patents.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su15054176/s1.

Author Contributions: A.C.L. contributed to the conceptualization of the project, supervision, writing the original draft of the manuscript and resource acquisition; A.S.L. contributed to the experimental investigation, formal analysis and writing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Universidad San Francisco de Quito USFQ Poligrants HUBI ID 17494, and the APC was funded by the Dean of Research.

Data Availability Statement: The data presented in this study are available in Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript or in the decision to publish the results.

References

- Jameel, A.T.; Muyubi, S.A.; Karim, M.I.A.; Alam, M.Z. Removal of Oil and Grease as Emerging Pollutants of Concern (EPC) in Wastewater Stream. *IIUM Eng. J.* 2011, 12, 161–169. [CrossRef]
- Yousefelahiyeh, R.; Dominic, C.C.S.; Ducoste, J. Modeling fats, oil and grease deposit formation and accumulation in sewer collection systems. J. Hydroinform. 2017, 19, 443–455. [CrossRef]
- 3. Kamyab, H.; Chelliapan, S.; Din, M.F.M.; Rezania, S.; Khademi, T.; Kumar, A. Palm Oil Mill Effluent as an Environmental Pollutant. In *Palm Oil*; Waisundara, V., Ed.; IntechOpen: Rijeka, Croatia, 2018; Chapter 2. [CrossRef]
- 4. Eljaiek-Urzola, M.; Romero-Sierra, N.; Segrera-Cabarcas, L.; Valdelamar-Martínez, D.; Quiñones-Bolaños, É. Oil and grease as a water quality index parameter for the conservation of marine biota. *Water* **2019**, *11*, 856. [CrossRef]
- Inyinbor Adejumoke, A.; Adebesin Babatunde, O.; Oluyori Abimbola, P.; Adelani-Akande Tabitha, A.; Dada Adewumi, O.; Oreofe Toyin, A. Water Pollution: Effects, Prevention, and Climatic Impact. In *Water Challenges of an Urbanizing World*; InTech: London, UK, 2018. [CrossRef]
- 6. Ahmed, T.; Zounemat-Kermani, M.; Scholz, M. Climate change, water quality and water-related challenges: A review with focus on Pakistan. *Int. J. Environ. Res. Public Health* **2020**, *17*, 8518. [CrossRef] [PubMed]
- Abbott, A.P.; Boothby, D.; Capper, G.; Davies, D.L.; Rasheed, R.K. Deep Eutectic Solvents Formed Between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids. J. Am. Chem. Soc. 2004, 126, 9142–9147. [CrossRef] [PubMed]
- 8. Bai, F.; Li, J.; Hua, C. Research Progresses of Deep Eutectic Solvents and its Application in Separation and Catalysis. *Mater. Sci. Forum* **2018**, *921*, 3–12. [CrossRef]
- 9. Sivabalan, V.; Sahith, J.K.; Lal, B. *Deep Eutectic Solvents as the New Norm for Oil and Gas Industry: A Mini Review*; Atlantis Press: Amsterdam, The Netherlands, 2021. [CrossRef]
- 10. Makoś-Chełstowska, P.; Słupek, E.; Małachowska, A. Superhydrophobic sponges based on green deep eutectic solvents for spill oil removal from water. *J. Hazard Mater.* **2022**, *425*, 127972. [CrossRef]
- 11. Safe Drinking Water Foundation. Oil Spills. Available online: https://www.safewater.org/fact-sheets-1/2017/1/23/oil-spills (accessed on 1 November 2022).
- 12. Płotka-Wasylka, J.; De la Guardia, M.; Andruch, V.; Vilková, M. Deep eutectic solvents vs. ionic liquids: Similarities and differences. *Microchem. J.* 2020, 159, 105539. [CrossRef]
- Smith, E.L.; Abbott, A.P.; Ryder, K.S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* 2014, 114, 11060–11082. [CrossRef] [PubMed]
- 14. Francisco, M.; González, A.S.; de Dios, S.L.G.; Weggemans, W.; Kroon, M.C. Comparison of a low transition temperature mixture (LTTM) formed by lactic acid and choline chloride with choline lactate ionic liquid and the choline chloride salt: Physical properties and vapour-liquid equilibria of mixtures containing water and ethanol. *RSC Adv.* **2013**, *3*, 23553–23561. [CrossRef]
- 15. Jablonsky, M.; Šima, J. Is it correct to name DESs deep eutectic solvents? *Bioresources* 2022, 17, 3880–3882. [CrossRef]
- 16. Kottaras, P.; Koulianos, M.; Makris, D.P. Low-transition temperature mixtures (LTTMs) made of bioorganic molecules: Enhanced extraction of antioxidant phenolics from industrial cereal solid wastes. *Recycling* **2017**, *2*, 3. [CrossRef]
- 17. Yu, Y.; Zhang, W.; Han, X.; Huang, X.; Zhao, J.; Ren, Q.; Luo, H. Menthol-based eutectic mixtures: Novel potential temporary consolidants for archaeological excavation applications. *J. Cult. Herit.* **2019**, *39*, 103–109. [CrossRef]
- Kareem, M.A. Novel Deep Eutectic Solvents and Their Application in the Liquid-Liquid Extraction of Aromatic Compounds. Ph.D. Thesis, University of Malaya, Kuala Lumpur, Malaysia, 2013.
- 19. An, Y.; Row, K.H. Evaluation of Menthol-Based Hydrophobic Deep Eutectic Solvents for the Extraction of Bisphenol A from Environment Water. *Anal. Lett.* **2021**, *54*, 1533–1545. [CrossRef]
- SMarullo, S.; Meli, A.; Dintcheva, N.T.; Infurna, G.; Rizzo, C.; D'Anna, F. Environmentally friendly eutectogels comprising l-amino acids and deep eutectic solvents: Efficient materials for wastewater treatment. *ChemPlusChem* 2020, *85*, 301–311. [CrossRef] [PubMed]

- 21. Florindo, C.; Monteiro, N.V.; Ribeiro, B.D.; Branco, L.C.; Marrucho, I.M. Hydrophobic deep eutectic solvents for purification of water contaminated with Bisphenol-A. *J. Mol. Liq.* **2020**, *297*, 111841. [CrossRef]
- Cruz, H.; Jordão, N.; Branco, L.C. Deep eutectic solvents (DESs) as low-cost and green electrolytes for electrochromic devices. *Green Chem.* 2017, 19, 1653–1658. [CrossRef]
- Škulcová, A.; Jablonský, M. Properties and thermal behavior of deep eutectic solvents based lactic acid. J. Hyg. Eng. Des. 2018, 25, 75–80.
- 24. Abuhasel, K.; Kchaou, M.; Alquraish, M.; Munusamy, Y.; Jeng, Y.T. Oilywastewater treatment: Overview of conventional and modern methods, challenges, and future opportunities. *Water* **2021**, *13*, 980. [CrossRef]
- 25. Henriksson, J. Characterization of Composition of the Fat-Rich Residues from Grease Separators; Linaeus University: Växjö, Sweden, 2016.
- 26. Páez-Flor, N. (Universidad de las Fuerzas Armadas, Quito, Ecuador). Personal communication, 2022.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.