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Research article

Efficient removal of lipophilic compounds from sewage sludge: Comparative evaluation of solvent extraction techniques

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ABSTRACT

Municipal sewage sludge, a by-product of wastewater treatment plants, presents environmental challenges due to its complex composition. Particular concern is the lipophilic and aliphatic compounds that pose risks to the environment and human health. This study focuses on the efficient removal of those compounds from sewage sludge using several organic solvents (hexane, toluene, chloroform, dichloromethane, acetone, hexane-methanol mixture, ethanol, and methanol) and ionic liquids (ILs) like tetrakis(hydroxymethyl)phosphonium chloride and 1-ethyl-3-methylimidazolium acetate by solvent extraction techniques. To determine optimal conditions, various factors such as solvent types, contact time, and temperature were examined. The results reveal that solvent polarity significantly impacts extract composition, with non-polar solvents like hexane and toluene yielding profiles characteristic of lipid-type compounds. An in-depth analysis of contaminants present in the sewage sludge was studied by Fourier-transform infrared spectroscopy (FTIR). Additionally, nuclear magnetic resonance (NMR) was used to identify the extracted compounds, including triglycerides, aliphatic esters, aliphatic alcohols, and free carboxylic acids. NMR provides data on the composition of the sewage sludge and indicates that among all the solvents used, tetrakis(hydroxymethyl) phosphonium chloride was the most suitable solvent for removing lipophilic and aliphatic compounds. Regeneration potential and reusability of the IL were conducted and verified by NMR. The results showed that tetrakis (hydroxymethyl) phosphonium chloride ionic liquid could be used for several extraction cycles. Identifying these compounds in the extracted mixture demonstrates that it adds value and potential for various applications. Towards environmental sustainability and circular economy, this effort develops strategies for the safe management, disposal, and recyclability of sewage sludge and, the reduction in environmental and health hazards associated with organic compounds.

1. Introduction

Municipal sewage sludge is a common by-product of wastewater treatment plants, generated during the process of treating domestic and industrial wastewater [1]. It poses multifaceted environmental challenges due to its complex composition, including high levels of organic and inorganic content, nutrient composition, and the potential presence of hazardous compounds [2–4]. Recent study

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showed that on an average 9–13 million tons of dry sewage sludge are produced in the European Union, whereas, numbers are nearly the same amount in the U.S.A., 30 million tons in China and about 4 million tons in India [5]. According to the European Environment Agency's recent report, among all EU countries, Germany produces the most sewage sludge (1.85 million tons) followed by the France (1.1 million tons), Spain (1.03 million tons) and Italy produced approximately 0.7 million tons annually [6,7]. Several approaches towards the sewage sludge disposal are: land-spreading, land-filling, incineration and composting. However, the high energy consumption and low profitability are the two major hurdles that hinder the wide application of conventional sewage sludge treatment technologies. Therefore, the uncollected sewage sludge waste and poorly disposed waste have significant health and environmental impacts. Among the concerns associated with sewage sludge, the presence of lipophilic compounds attracts attention as a significant threat to the environment and human health [8–10].

Lipophilic compounds in sewage sludge involve a wide range of organic pollutants, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, pharmaceuticals, personal care products etc. [11,12]. These compounds enter wastewater treatment plants through various sources, such as domestic and industrial discharges. Due to their insolubility in water and affinity for organic matter, low concentration, diversity, and unique chemical properties, lipophilic compounds become entrapped within the sewage sludge during the treatment process.

The lipophilic compounds in sewage sludge raises concerns due to their potential persistence in the environment which has the ability to bioaccumulate in organisms, and adversely effect on ecosystems and human health [13,14]. If properly not managed, the disposal of sewage sludge can lead to the release of the said compounds into the environment, resulting in contamination of soil and water bodies, and potentially entering the food chain, ultimately affecting the human life [15–17].

In this direction, to manage the potential risks associated with lipophilic compounds in sewage sludge, effective management strategies are necessary. The removal of lipophilic compounds from sewage sludge is a crucial step in reducing their environmental impact and safeguarding human health. There are several methods like adsorption, membrane separation, complex formation, degradative solvent extraction, direct solvent extraction etc. available to remediate these compounds from sewage sludge [18–21]. Among all the process, the direct solvent extraction as well as degradative solvent extraction methods have emerged as a promising technique for the removal of lipophilic compounds. Degradative solvent extraction technique involves the use of a solvent to dissolve and decompose the lipophilic compounds under high temperature and pressure, and/or in the presence of a catalyst. Many researchers have employed degradative solvent extraction utilizing 1-methylnaphthalene as a solvent to treat sewage sludge and biomass [22,23]. However, this process presents several drawbacks, including high energy consumption, challenges in solvent handling and recovery, and catalyst deactivation [24,25]. On the other hand, the direct solvent extraction is simple process, operates at lower temperatures and pressures compared to degradative solvent extraction [26].

Direct solvent extraction involves the use of organic solvents with high affinity for lipophilic compounds to selectively extract and separate them from the sludge matrix [27,28]. By employing appropriate solvents and extraction conditions, a significant portion of lipophilic compounds can be targeted and removed, thereby reducing their presence in sewage sludge. Additionally, characterization of the extracted compounds provides valuable insights into their identity, composition, and potential risks. By understanding the presence and nature of these compounds in sewage sludge, we can advance towards sustainable waste management practices and protect both the environment and human well-being. Implementing effective removal strategies for lipophilic compounds in sewage sludge is crucial to ensure the protection of the environment and mitigate potential risks to human health.

In the current study, the main goal was to efficiently remove lipophilic and aliphatic compounds from sewage sludge using solvent extraction techniques. The effectiveness of various conventional solvents, including methanol, ethanol, acetone, hexane-methanol, hexane, toluene, chloroform and unconventional yet greener solvents like tetrakis(hydroxymethyl) phosphonium chloride, and 1-ethyl-3-methylimidazolium acetate ionic liquids were evaluated for their ability to remove the lipophilic and aliphatic compounds. In addition, nuclear magnetic resonance (NMR) spectroscopy was employed as an analytical tool to identify and characterize the extracted compounds, which include triglycerides, aliphatic esters, aliphatic alcohols, and free carboxylic acids. The research findings of the current study contribute to the development of efficient strategies for the safe management and disposal of municipal sewage sludge, with the aim of reducing the environmental and health hazards associated with lipophilic and aliphatic compounds.

2. Materials and methods

2.1. Chemical reagents

HPLC grade methanol, hexane (anhydrous, 95 %), toluene (anhydrous, 99.8 %), chloroform (anhydrous, ≥99 %), chloroform-d (99.8 atom % D), 1-ethyl-3-methylimidazolium acetate, and tetrakis(hydroxymethyl)phosphonium chloride solution, glucose (99 %), Bovine serum albumin (98 %), vanillin (99 %), copper sulfate (99 %) were purchased from Sigma-Aldrich. Other chemicals used in this work were purchased from different suppliers - phenol (Chempur, 99.0 %), sulphuric acid (VWR Chemicals, 97.0 %), sodium hydroxide (AppliChem, 99 %), sodium chloride (Merck, 99.9 %), potassium sodium tartrate tetrahydrate (Supelco, 99.0 %), Folin-Ciocalteau reagent (Chempur), potassium dihydrogen phosphate (Chempur, 99.5 %), potassium chloride (Scharlau, 99 %), sodium carbonate (Scharlau, 99.5 %), disodium hydrogen phosphate (AppliChem, 99.0 %), sodium hydroxide (AppliChem, 99 %), anhydrous sodium sulfate. Olive oil (Acros Organics, pure), ortho-phosphoric acid (Chempur, analytical grade). Ethanol was obtained from Kalsnavas Elevators SIA, Latvia. All the chemicals acquired are of analytical standard and used without any additional purification step.

2.2. Sample collection and preparation

The primary municipal sewage sludge was collected from the biological wastewater treatment plant located in Riga, Latvia (>100 000 Population Equivalent, BAS "Daugavgriva"). The sludge samples were collected in polyethylene bottles and stored at −20 °C prior to any use. Then the collected sludge was centrifuged at 5000 rpm for 15 min to dewater the sludge. The dewatered sludge was then dried in an oven at 100 °C overnight. The resultant sewage sludge was ground using a mortar and pestle and finally, the sludge was stored at 4 °C prior to further studies.

2.3. Characterization of physicochemical parameters

Carbohydrate, protein and lipid content in primary municipal sewage sludge samples was determined spectrophotometrically by using conventional methods.

The content of total carbohydrates was determined by the phenol-sulphuric acid method [29]. Prior to analysis, sulphuric acid (3 %) was added to the sludge samples, followed by autoclave treatment at 121 °C for 15 min. The obtained supernatant was analyzed at 490 nm using glucose solutions as the reference.

Protein content was determined by the Lowry method which is based on the interactions between peptide bonds (present in proteins) and copper (present in Lowry reagents) [30]. Reagents were prepared according to Shen et al. [31]. Prior to analysis, ultrasonication (130 W, 20 kHz, 30 % amplitude, 2 min) was applied to the sludge samples, followed by heating for 15 min. The obtained supernatant was analyzed at 750 nm using bovine serum albumin solutions as the reference.

Lipid content was determined by the sulfo-phospho-vanillin method [32]. Prior to analysis, ultrasonication was applied to the sludge samples (130 W, 20 kHz, 30 % amplitude, 1 min), followed by adding chloroform and methanol, then mixing vigorously. The chloroform layer was collected separately and heated to evaporate the solvent. Finally, sulphuric acid (concentrated) was added and the solution was heated until it appeared brown. 10 min after adding phosphovanillin reagent, the sample solution was analyzed at 530 nm using olive oil as the reference compound.

Percentage of total solids (TS) was determined by drying the samples at 105 °C for 12 h. Content of fixed and volatile solids (FS and VS, respectively) was determined by heating the samples at 550 °C for 4 h.

2.4. Removal of lipophilic compounds

2.4.1. Soxhlet extraction method

The removal of lipophilic compounds from the municipal sewage sludge was conducted in Soxhlet extraction apparatus using several organic solvents such as acetone, ethanol, hexane, toluene, chloroform, and methanol [33–35]. Approximately 1 g of sludge was taken in a cellulose thimble, and then the extraction was conducted with varying temperature of 40–80 °C, and treatment time of 2–8 h. After the process was completed, the lipophilic compounds were separated by evaporating the solvents at 40 °C using a rotary evaporator. The percentage of lipophilic compound was calculated by following equation.

$$\textbf{\textit{Yield of extract}}\ \% = \frac{\textbf{\textit{Mass of oil}}\ (\boldsymbol{g})}{\textbf{\textit{Mass of dry sludge}}\ (\boldsymbol{g})} \times \mathbf{100} \tag{1}$$

2.4.2. Extraction of lipophilic compounds using ionic liquids

Extraction of lipophilic compounds was carried out by using two different kinds of ionic liquids (tetrakis(hydroxymethyl) phosphonium chloride, and 1-ethyl-3-methylimidazolium acetate. In typical removal procedure, 10 mL ionic liquids were added to 1 g dry sludge sample and the mixture was heated up to 100 °C for 8 h with a magnetic stirrer. After completion of the experiment, the mixture was allowed to cool down to room temperature followed by the addition of methanol (10 mL). The obtained mixture was then placed in a separating funnel by adding 5 mL hexane. The upper hexane phase containing lipophilic compound was then washed with distilled water (10 mL) to remove trace polar compounds. The hexane phase was dried with anhydrous sodium sulfate and evaporated in rotary evaporator. The resultant sample was dried under vacuum for 24 h and weighed afterwards. The yield of the extract was calculated by equation (1).

2.5. Instrumentation techniques

The moisture in primary sewage sludge was analyzed by moisture analyzer Kern DBS 60-3 (Germany). The sludge samples were centrifuged for several studies by using OHaus Frontier centrifuge, model 5718R (Germany). The sonication process was done by Cole Parmer 130-Watt ultrasonic processor (Canada). The concentration of carbohydrates, proteins and lipids in the sludge samples was measured by Genesys 150 (Thermo Scientific, UK) UV/Vis spectrophotometer. The lipophilic compounds in sewage sludge extract was characterized by ^{1}H and ^{13}C NMR, model Bruker Avance 500 spectrometer.

3. Results and discussions

3.1. Physicochemical parameters

The current paper represents our recent efforts to remove and characterize the lipophilic as well as aliphatic substances from primary sewage sludge. In this direction, we have employed several conventional methods for detecting physical parameters along with content of lipid, protein and carbohydrate in the sludge and the results are presented in Table 1. Content of fixed and volatile solids (FS and VS, respectively) was found to be 22.6 % and 77.4 %, respectively. The carbohydrate was found to be 10 % in the primary sludge which is coherent with the literature [36]. The protein content was found to be approximately 23.9 %. Similar findings were reported by Shana et al. [37]. Lipid analysis was performed according to sulfo-phospho-vanillin (SPV) method with olive oil as the reference compound and 9.1 % was detected in Latvian sewage sludge by this method. All the analyses were performed in triplicate. Results are presented as mean value ± standard deviation. After analysis of all the components in primary sewage sludge, lipophilic substances were removed by using different kind of solvents and characterized through NMR. Lipophilic substances are harmful if not treated appropriately, on the other hand, they are very important class of value-added products in several cases as they can be used in a number of applications such as biofuel production, cosmetic, pharmaceuticals, chemical industries, animal feed etc. [38].

3.2. Effects of various parameters on the removal process

Fig. 1A shows the percentage of lipophilic compounds removed from sewage sludge by using different organic solvents such as methanol, tetrakis(hydroxymethyl) phosphonium chloride, 1-ethyl-3-methylimidazolium acetate, ethanol, acetone, hexane-methanol, hexane, toluene, and chloroform. From the figure, it is evident that among all the solvents, ethanol appears to be the least effective in removing lipophilic compounds. Conversely, the ionic liquid tetrakis(hydroxymethyl) phosphonium chloride demonstrates the highest efficiency in extracting these compounds, with an extraction yield of approximately 12 %. On the other hand, 1-ethyl-3-methylimidazolium acetate ionic liquid could remove 8 % of lipophilic compounds. The ILs are the green replacements for harmful volatile organic solvents due to their non-volatile character, excellent chemical and thermal stability, potential recoverability, and design possibilities [40]. The higher yield by ILs might be due to the fact that direct dissolution of sludge in ionic liquids could lead to the recuperation of more lipophilic components such as free carboxylic acids, wax/gum and aliphatic alcohols. Apart from ILs, the mixture of hexane and methanol also showed good efficiency to remove lipophilic compounds which was about 8.82 %. Therefore, for further study (effect of time), solvents like methanol, hexane, mixture of methanol and hexane, and tetrakis(hydroxymethyl) phosphonium chloride were chosen.

To know the effect of contact time on lipophilic substance removal capacity, solvents like hexane, methanol, the mixture of methanol-hexane, and IL were taken and the separation process was conducted by varying the time from 1 to 10 h (Fig. 2). It was found that the removal percentage was increased with increasing reaction time for all the studied solvents. The maximum yield with IL was reached at the time of 8 h, whereas the maximum yield for the methanol-hexane was reached at the time of 6 h. From the effect of time, it is concluded that the IL is the best solvent to separate the highest amount of lipophilic compounds from the municipal sewage sludge. Keeping this in mind, IL was further studied for the effect of temperature on the separation process.

Fig. 3 shows the effect of temperature (80–160 °C, at constant time of 6 h) on the separation of lipophilic and aliphatic compounds from the sludge by using tetrakis(hydroxymethyl)phosphonium chloride IL. It was observed that at the temperature of 80 °C the separation process started but the yield was very low at about 4 %. Upon increasing the system temperature, the yield increased and equilibrium was achieved at 100 °C. Further increase in temperature did not affect the percentage of lipid extraction. From the effect of temperature, it can be said that the separation process of lipophilic substances using IL is endothermic in nature.

3.3. Characterization of sludge by FTIR

After the removal of lipophilic compounds by different solvents, it was evident that the mixture of hexane and methanol was the best solvent to remove the highest amount of lipophilic substances. Therefore, we have characterized the leftover sludge (hexane, methanol, and mixture of hexane-methanol) by FTIR spectroscopy to check the functional groups present in it (Fig. 4). In the figure many sharp and broad peaks are visible which correspond to several functional groups like O-H, C=O, C-C, C-H, and N-H. The peak at

Table 1
Properties of primary sewage sludge collected from Latvian wastewater treatment plant [39].

Properties of primary sludge	Values
Dry weight	2.5 ± 0.5 % of wet weight
Volatile solids	77.4 ± 1.0 % dry weight
Fixed solids	22.6 ± 1.0 % dry weight
Carbohydrate	10.0 ± 0.1 % dry weight
Protein	23.9 ± 0.3 % dry weight
Lipid	9.1 ± 0.9 % dry weight

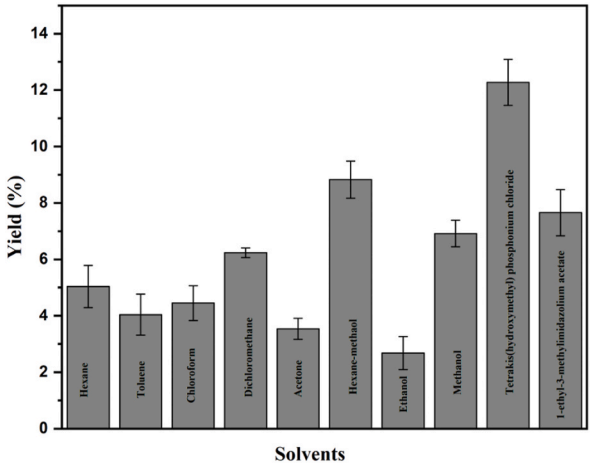

Fig. 1. Effect of solvents on removal of lipophilic compounds from sewage sludge, arranged with respect to the polarity of the solvents used for the extraction: starting with the less polar hexane extract followed by toluene, chloroform, dichloromethane, acetone, hexane-methanol mixture, ethanol, methanol, followed by extracts of ionic liquids tetrakis(hydroxymethyl)phosphonium chloride and 1-ethyl-3-methylimidazolium acetate.

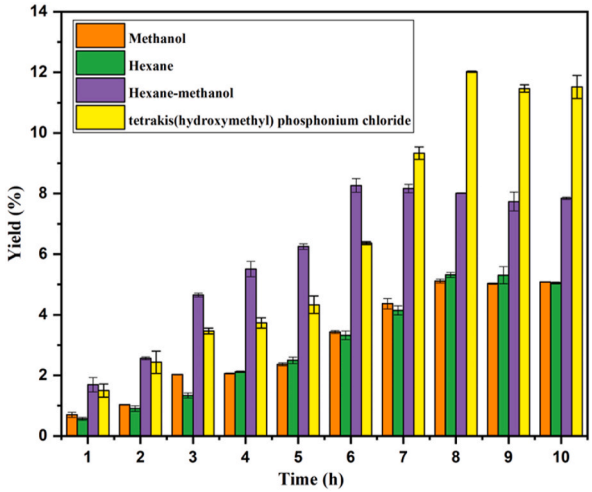

Fig. 2. Effect of time on removal of lipophilic compounds from sewage sludge.

3400 cm^{-1} corresponds to the stretching vibration of the O-H group which may be due to the presence of polyalcohol and saccharides. The duplet band at ~2900 cm^{-1} referred to the stretching vibration of the C–H bond. In region ~1650 cm^{-1}, the signal reflects stretching, and asymmetrical vibrations of COO− which are the characteristic peaks for peptides and proteins. Additionally, the band at ~1540 cm^{-1} corresponds to symmetrical vibrations of the R_3-N^+H bond, characteristic of proteins. Absorption bands were also observed near 1465 cm^{-1}: monosaccharides (deforming C–H bond vibration), alkenes (═CH functional group), and amides (N–H group) [41]. The last analyzed peak at ~1030 cm^{-1} is a characteristic peak for C–O stretching vibration in glycerol. This peak confirms the presence of fats and fatty acids in the sample even after removing most of the lipophilic compounds through organic solvents.

3.4. Characterization of lipophilic compound through NMR analysis

All extracted samples were analyzed by NMR spectroscopy, ^{1}H NMR spectra in Figs. 5 and ^{13}C NMR spectra in Fig. 6. The polarity value (E_T^N) of all the solvents used are taken from literature [42]. The spectra clearly indicate the impact of the polarity of the solvent on the composition of the extract. When a non-polar solvent (hexane and toluene) is used, the recorded spectra were typical for lipid type compounds like triglycerides, free fatty acids, alcohols and waxes. The typical corresponding signals are as follows: 1) characteristic multiplets in the region 1.82–0.55 ppm in ^{1}H NMR spectra (Fig. 5), and 43-11 ppm in ^{13}C NMR spectra (Fig. 6) are assigned for long aliphatic chains, 2) two doublets at 4.28 ppm ($J = 12.3$ Hz and $J = 4.7$ Hz) are assigned to CH_2O moiety in glycerin residue and clearly indicates the presence of the triglycerides, 3) the triplet at 4.04 ppm ($J = 6.4$ Hz) is characteristic for the alcohol residues in aliphatic esters like waxes, 4) a multiplet at 3.68–3.53 ppm is characteristic to $HOCH_2$ in alcohols, thus herein these signals give evidence for

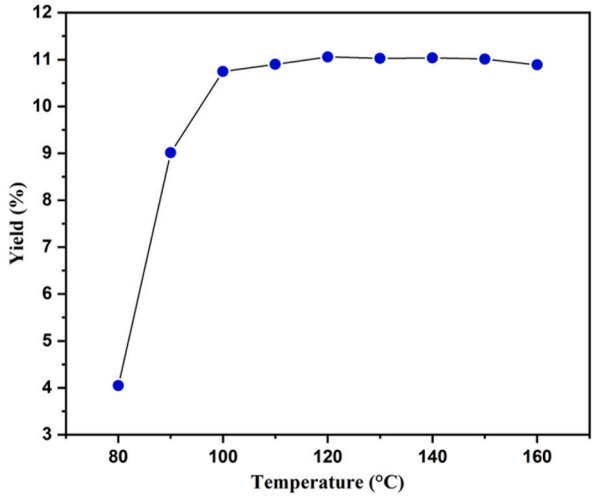

Fig. 3. Effect of temperature on the removal of lipophilic compounds from sewage sludge by tetrakis(hydroxymethyl)phosphonium chloride IL.

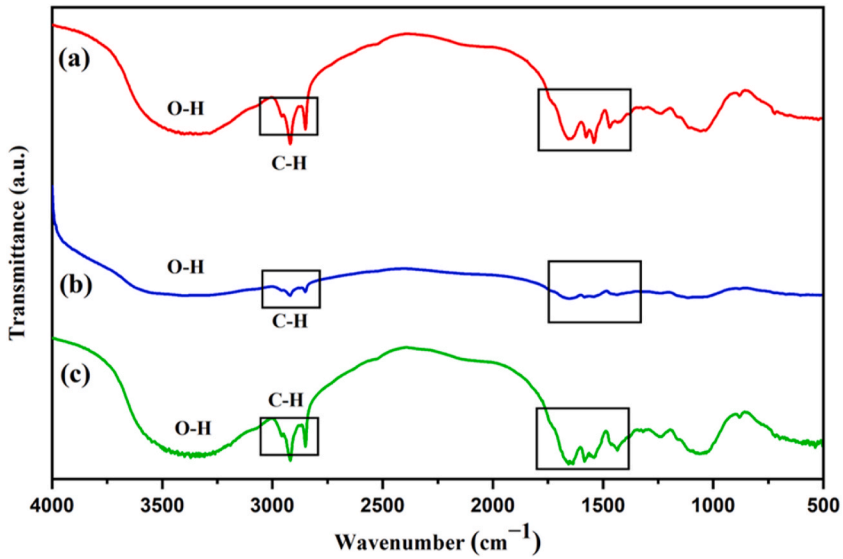

Fig. 4. FTIR spectrum of sewage sludge after removal of lipophilic compounds by a) hexane, b) methanol, and c) mixture of hexane-methanol.

fatty alcohols and 5) the multiplet at 2.42–2.22 is typical for CH_2 protons next to carbonyl group – these signals are assigned both for carboxylic acids and esters. These extracts contain various unsaturated residues as it is provided from the spectra: 1) a multiplet at 5.42–5.27 ppm corresponds to the vinyl group and 2) the triplet at 2.76 ppm ($J = 6.1$ Hz) and a multiplet at 2.09–1.92 ppm characteristic to allylic and *bis*-allylic positions, respectively. The presence of the carboxylic acids in hexane extract is smoothly showed by a high intensity signal at 179 ppm in ^{13}C NMR spectrum. Remarkably less intensive and pronounced signal is detected at 173–174 ppm which is assigned to ester type carbonyl group. The toluene extract is characterized with low intensity signals both at 180 and 170 ppm characteristic to carboxylic acids and esters, respectively. Strong signals at 130 ppm assigned for vinyl groups are detected in the toluene extract.

Even a slight increase of the solvent polarity demonstrates an influence to the composition of the extract. Low intensity signals at 6.0 and 6.7 ppm and 7.1–8.0 ppm are detected in the ^1H NMR spectra for the chloroform and dichloromethane extracts. These signals may give evidence for the presence of various aromatic, including phenol type compounds. It should be admitted that the relative intensity is increased for the signal at 3.6 ppm which may be attributed to the presence of various medium and long chain alcohols (it is expected that low chain alcohols have been volatilized during the preparation of the extract). Besides the intensity of the signal at 2.7 ppm has been considerably decreased. This signal is characteristic for the *bis*-allylic positions e.g. in fats: thus it can be speculated that the unsaturation degree for the extracts is reduced. The signals (127–130, 149 and 169–173 ppm) characteristic for the aromatic compounds are detected in the ^{13}C NMR spectra, too.

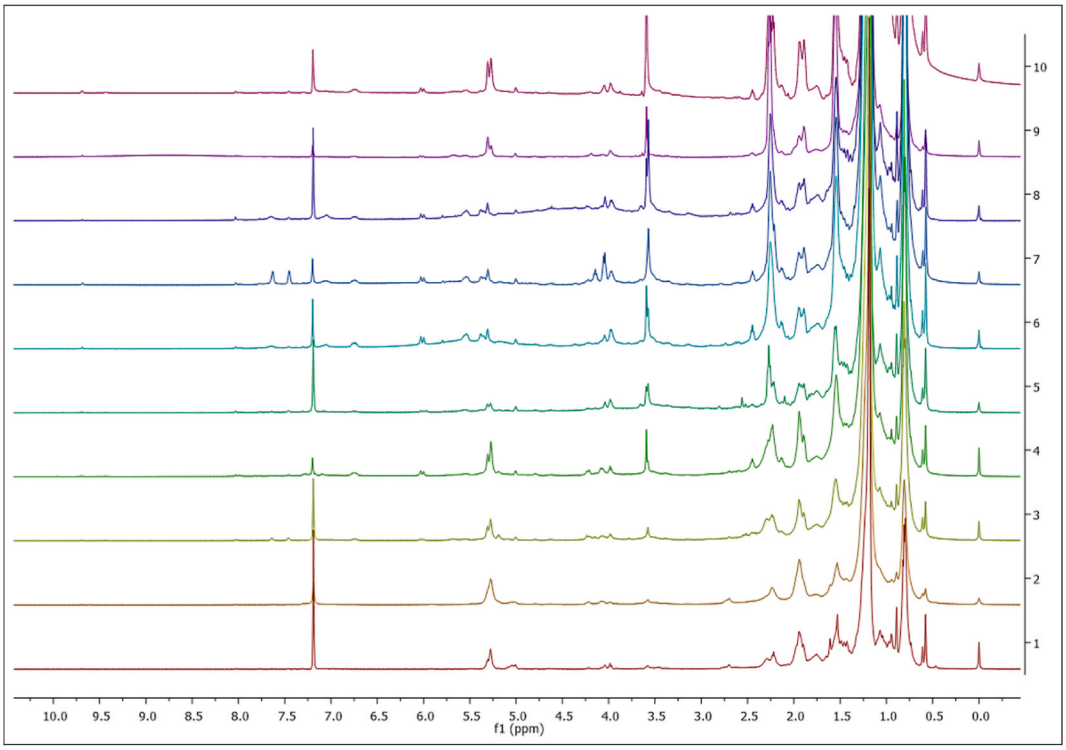

Fig. 5. ^{1}H NMR spectra for various sewage sludge extracts ($CDCl_3$, 500 MHz). All spectra are arranged with respect to the polarity of the solvents used for the extraction: starting with the less polar 1 -hexane extract ($E_T^N = 0.009$), followed by 2 - toluene ($E_T^N = 0.099$), 3 - chloroform ($E_T^N = 0.259$), 4 - dichloromethane ($E_T^N = 0.309$), 5 - acetone ($E_T^N = 0.355$), 6 - hexane-methanol mixture, 7 - ethanol ($E_T^N = 0.654$) and 8 - methanol ($E_T^N = 0.762$) extracts, followed by extracts of ionic liquids - 9 - tetrakis(hydroxymethyl)phosphonium chloride (THPC) and 10 - 1-ethyl-3-methylimidazolium acetate (EMIM OAc).

The character of the ^{1}H NMR spectrum of the acetone extract is even more diverse which gives evidence for a different composition of this extract in comparison with the hexane extract which could be considered as typical for lipophilic extracts. There are no signals characteristic to the glycerol residue in triglycerides. Besides it should be admitted that the unsaturation caused by the presence of isolated vinyl groups is reduced too. The intensity of these signals is reduced and the character of them is changed.

Besides different signals at 0.5–2.5 ppm representing various aliphatic fragments, the small, various intensity signals at 3.4–8.15 ppm are typical for the ethanol and methanol extracts in ^{1}H NMR spectra. The last group of signals might be attributed to the presence of various polar functional groups. Signals with high intensity at 3.6 ppm may be assigned to the presence of alcohols. The chemical shifts in the weaker fields are characteristic to various aromatic compounds. Similarly, the character of the signals in the aromatic region is changed in the ^{13}C NMR spectrum: several signals at 127–133, 147 and 167 ppm characterizing the aromatic core may be assigned, besides the ^{13}C spectra gives evidence for the presence of various types of carboxylic acid derivatives (characteristic signals at 173–174 and 179 ppm). As expected, the hexane-methanol extracts contain compounds which are characteristic both for non-polar and highly polar extracts.

The extracts obtained by extraction with ionic liquids contain both aliphatic, lipophilic compounds (similar to those obtained when extraction was run with hexane or toluene) as well as some of the compounds detected in alcohol extracts. It should be admitted that the extracts contain mainly alcohols, waxes and free acids from lipophilic compounds, whereas the signals characteristic for the glycerol residue in the triglycerides is not convincing. The THPC is characterized with a pronounced signal at 180 ppm in ^{13}C NMR spectrum representing free acids, contrary to the EMIM OAc extract which contains various carboxylic acid derivatives.

3.5. Reusability study

The removal capacity and regeneration properties are two key parameters to evaluate suitable solvents. An ideal solvent should not only possess higher extraction capability, but also show better reusability properties, which will significantly reduce the overall cost of the process. In order to make the removal of lipophilic compounds more economical and feasible, regeneration potential and reusability of tetrakis(hydroxymethyl) phosphonium chloride was studied. To verify the reusability of the ionic liquid after removal process, NMR spectroscopy was used. The provided extraction procedure does not cause degradation of the ionic liquids: both before and after extraction a singlet at 4.5 ppm assigned for CH_2 group is detected in the ^{1}H NMR spectra (Fig. 7). Some impurity signal is detected at 1.3 and 3.1 ppm after extraction, thus the tetrakis(hydroxymethyl) phosphonium chloride ionic liquid could be used for

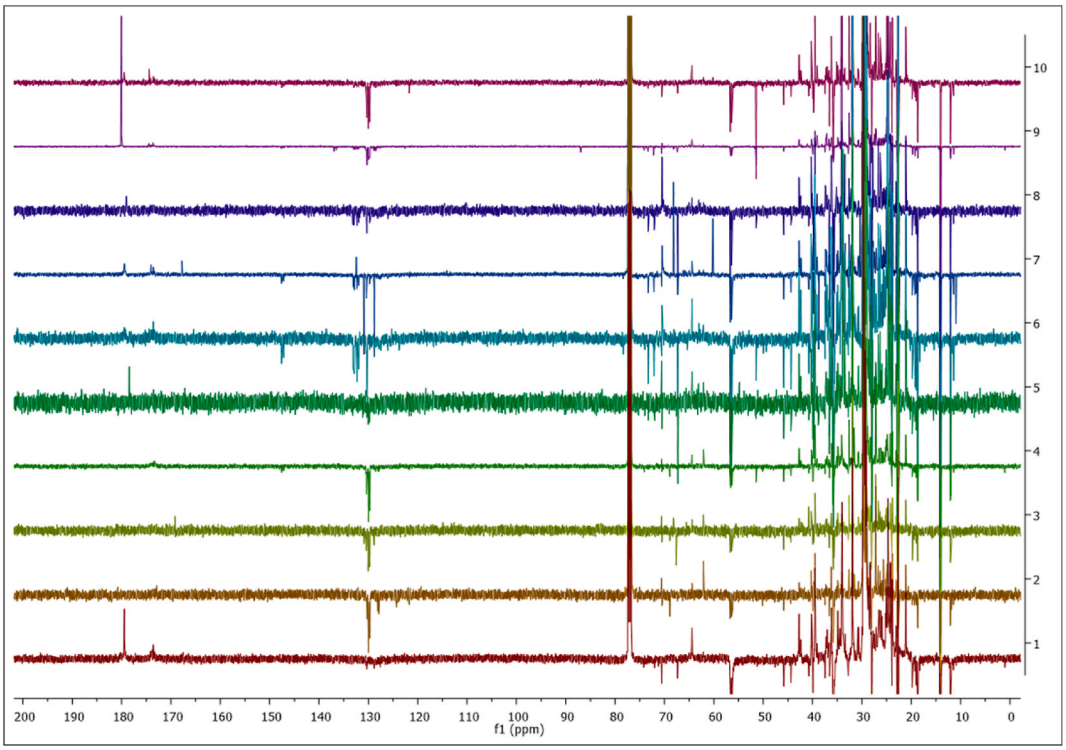

Fig. 6. ^{13}C NMR spectra for various sewage sludge extracts ($CDCl_3$, 125 MHz). All spectra are arranged with respect to the polarity of the solvents used for the extraction: starting with the less polar 1 -hexane extract ($E_T^N = 0.009$), followed by 2 - toluene ($E_T^N = 0.099$), 3 - chloroform ($E_T^N = 0.259$), 4 - dichloromethane ($E_T^N = 0.309$), 5 - acetone ($E_T^N = 0.355$), 6 - hexane-methanol mixture, 7 - ethanol ($E_T^N = 0.654$) and 8 - methanol ($E_T^N = 0.762$) extracts, followed by extracts of ionic liquids - 9 - tetrakis(hydroxymethyl)phosphonium chloride (THPC) and 10 - 1-ethyl-3-methylimidazolium acetate (EMIM OAc).

next extraction cycles for the same material (organic substances).

The implementation of a solvent extraction method for the removal of organic components from sewage sludge marks a significant advancement in sludge management practices. This innovative approach offers several key benefits, ultimately contributing to more sustainable and environmentally friendly wastewater treatment processes. Selective extraction of organic compounds from the sludge not only reduces the overall volume of the sludge but also enhances its quality for subsequent treatment or disposal. From the ^{1}H and ^{13}C NMR results it is concluded that the tetrakis(hydroxymethyl) phosphonium chloride is the best solvent to extract a higher amount of both aliphatic and lipophilic compounds compared to the other solvents tested. The reduction in organic (aliphatic and lipophilic) content leads to a more stabilized sludge, lowering the potential for unpleasant odors and mitigating the environmental risk. Additionally, the extracted organics can be further processed or utilized, potentially creating new ways for resource recovery and minimizing the environmental footprint associated with traditional sludge disposal methods.

In addition, the solvent extraction (using ILs) method aligns with broader environmental goals, promoting the circular economy and sustainable practices in wastewater treatment. The reduction in sludge volume not only streamlines the disposal process but also opens up opportunities for the beneficial reuse of the treated sludge in various applications, such as agricultural soil conditioning or energy generation. Furthermore, ILs can be recycled and reused for organic compounds extraction. This approach reflects a commitment to responsible waste management, addressing both the challenges of sludge disposal and the potential for extracting value from waste products.

4. Conclusions

The purpose of the present study was to remove the lipophilic compounds from sewage sludge by using several organic solvents. The identification and quantification of the above mentioned products can contribute to the development of efficient tactics for resource recovery from wastewater treatment plants, and promoting a more sustainable approach to waste management. The ionic liquid [tetrakis(hydroxylmethyl) phosphonium chloride] was able to remove a higher amount of lipophilic and aliphatic compounds as compared to the other organic solvents such as methanol, hexane, toluene, acetone, dichloromethane, chloroform and ethanol used in standard Soxhlet extraction methods. The ionic liquid was found to be the most suitable solvent to remove the highest amount (more than 12 %) of organic compounds from primary sludge. Most of the separated compounds were free carboxylic acids, and aliphatic alcohols (fatty alcohols), accounting for more than 90 % of the total lipids. Due to their diverse properties and applications, free

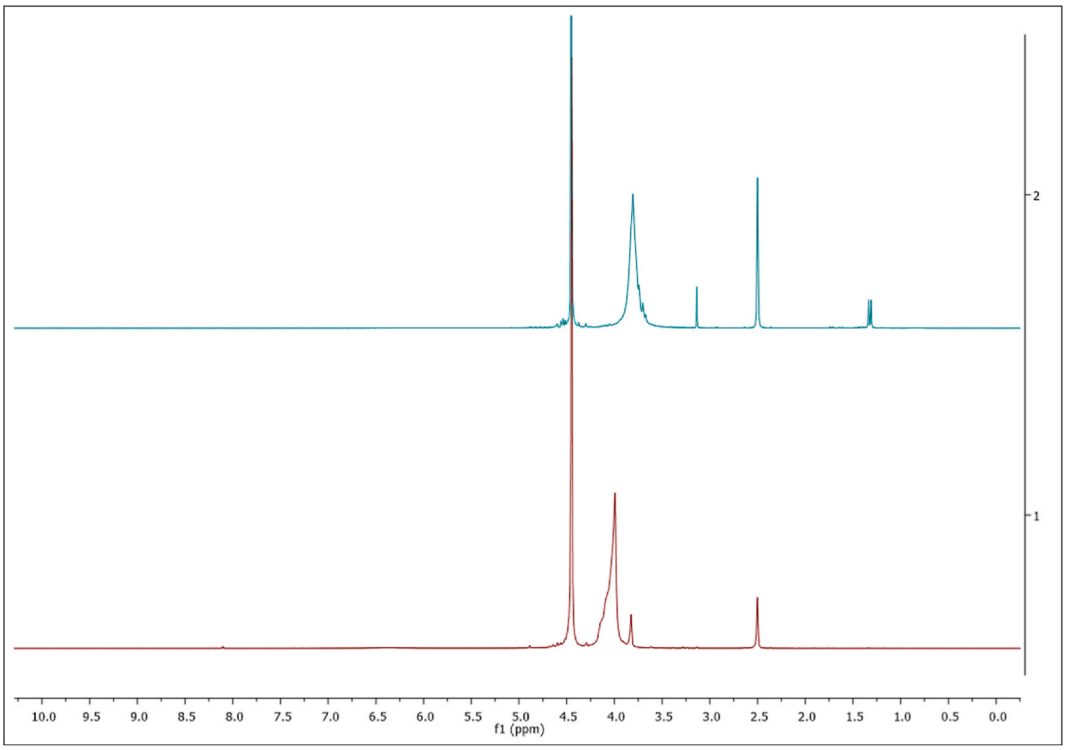

Fig. 7. ^{1}H NMR spectra for tetrakis(hydroxymethyl) phosphonium chloride (500 MHz, DMSO-d_6 + D_2O) before (1) and after (2) extraction.

carboxylic acids and free fatty alcohols are widely used in industries like cosmetics, personal care products, food and pharmaceuticals, chemicals, and textiles. Consequently, these compounds can be extracted from sludge and applied across various fields. Additionally, this work shows the clear benefits of ^{13}C and ^{1}H NMR techniques applied to the characterization of municipal sewage sludge. Overall, the solvent extraction method using ionic liquid as a greener solvent presents a transformative step forward in optimizing sludge management strategies, with positive implications for both the efficiency of wastewater treatment plants and their environmental impact.

CRediT authorship contribution statement

Basanti Ekka: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Inese Mierina:** Writing – review & editing, Methodology, Formal analysis. **Ruta Zarina:** Writing – review & editing. **Linda Mezule:** Writing – review & editing, Project administration, Funding acquisition.

Data availability statement

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declaration of competing interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all authors listed and there are no other persons who satisfied the criteria for authorship. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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