

Uncovering the impact of metals on the formation and physicochemical properties of fat, oil and grease deposits in the sewer system

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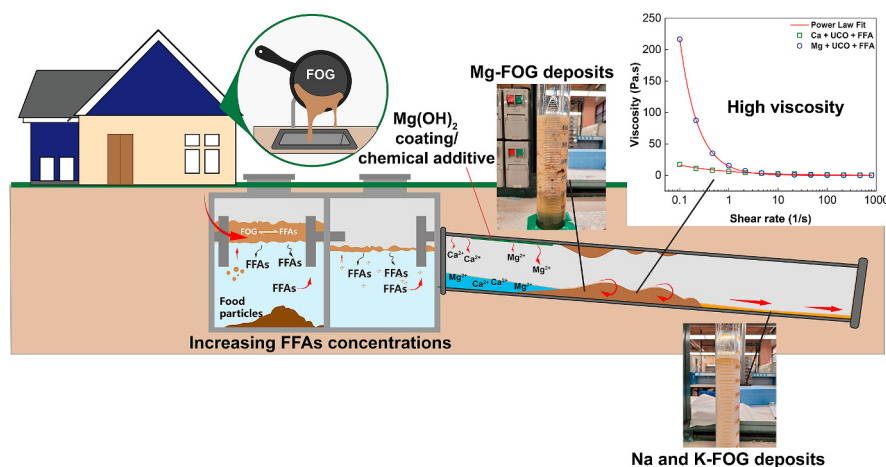
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HIGHLIGHTS

- Mg ion produced the highest FOG deposits with increased free fatty acids content.
- Low solubility of Mg source enhanced FOG deposition via aggregation reaction.
- Mg-FOG deposits show high apparent viscosity and consistency index.
- Na and K-FOG deposits are less likely to contribute to sewer blockage.
- The use of $\text{Mg}(\text{OH})_2$ for anti-corrosion could promote FOG deposition in sewers.

GRAPHICAL ABSTRACT



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ABSTRACT

The deposition of fats, oil, and grease (FOG) in sewers reduces conveyance capacity and leads to sanitary sewer overflows. The major contributing factor lies in the indiscriminate disposal of used cooking oil (UCO) via kitchen sinks. While prior investigations have mostly highlighted the significance of Ca^{2+} from concrete biocorrosion, the influence of common metal ions (e.g., Mg^{2+} , Na^+ , K^+) found in kitchen wastewater on FOG deposition has received limited attention in the existing literature. This study aimed to elucidate the roles of Ca, Mg, Na and K in FOG deposition in sewers and examine the influence of metal ions, fat/oil sources, and free fatty acids (FFAs) on the physicochemical and rheological properties of FOG deposits. To examine FOG deposit formation, synthetic wastewater containing 0.1 g/L of each metal ion was mixed with 40 mL of fat/oil and agitated for 8 h. Following FOG deposition, three distinct phases were observed: unreacted oil, FOG deposit and wastewater. The composition of these phases was influenced by the composition of metal ions and FFA in the wastewater. Mg produced

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the highest amount of FOG of 242.5 ± 10.6 mL compared to Ca (72.5 ± 3.5 mL) when each FFAs content in UCO was increased by 10 mg/mL. Molar concentration, valency and the solubility of metal ion sources were identified to influence the formation of FOG deposits via saponification and aggregation reaction. Furthermore, Fourier-Transform Infrared spectroscopy indicated that the FOG deposits in this study were similar to those collected from the field. This study showed that the use of $\text{Mg}(\text{OH})_2$ as a biocorrosion control measure would increase FOG deposition and highlights the need for a comprehensive understanding of its roles in real sewage systems.

1. Introduction

The accumulation of fats, oils and grease (FOG) deposits in sewer systems is driven by various mechanisms, including saponification, aggregation and crystallisation involving free fatty acids (FFAs) and metal ions (He et al., 2013). This phenomenon has long been recognised as a significant cause of sewer blockages, leading to sanitary sewer overflows (SSOs) (Gao et al., 2023). For instance, Yarra Valley Water in Australia reported over 1300 blockages in 2022 due to improper disposal of items like used cooking oil (UCO) in kitchen sinks, which is worsened by the combination of wet wipes and other hygiene products in toilets, resulting in an annual expenditure of approximately AUD\$1 million for the removal of blockages (Chris, 2023). Similarly, Thames Water in the UK encountered massive FOG deposits, including a 10-tonne “elephant-sized” deposit in 2020 and a mammoth fatberg the size of a bungalow in a Canary Wharf sewer in 2021 (Thames Water, 2020, 2021). The recurring nature of these blockages highlights the urgent need for proactive solutions to alleviate the significant operational and financial burden faced by the wastewater industry (Wallace et al., 2017).

To develop a sustainable FOG management approach, an in-depth understanding of the mechanisms and components involved in FOG deposit formation is essential (He et al., 2017). Major components such as FOG, FFAs, Ca, suspended solids, and water play important roles in FOG deposition, with the sources of the FOG and FFAs significantly affecting the physicochemical properties of the deposits (Yusuf et al., 2023). Deep-frying is a common practice in households and food service establishments (FSEs) (Adhikesavan et al., 2022). The process promotes a series of reactions, including hydrolysis, which increase the FFA content (Omidvar et al., 2022). Once cooking oil is used multiple times, it is classified as UCO. The continued use of such oil is discouraged due to potential health risks, underscoring the importance of its proper disposal (Chen et al., 2013). However, proper disposal is not common, leading to the formation of FOG deposits.

Wastewater industries globally have been advocating for residential users and FSE operators to follow the guidelines set forth in UCO disposal campaigns. These guidelines include allowing the oil to cool, pouring it into a plastic container, and then disposing of it in a food waste bin instead of down the kitchen sink. Despite these efforts, the campaigns have yet to achieve complete success, as the problem of sewer blockages caused by FOG accumulation continues, indicating that improper disposal of UCO via kitchen sinks is still prevalent (Wallace et al., 2017). The improper disposal of UCO has been linked to the formation of highly viscous and adhesive FOG deposits in the presence of Ca^{2+} , which resists wastewater flow within sewer networks (Omidvar et al., 2022). These deposits create a congealing point for other materials, such as wet wipes and sanitary items, ultimately forming fatbergs (Ahmad et al., 2022). A high content of palmitic (C16:0), oleic (C18:1) and stearic acid (C18:0) has been identified as the primary cause of these FOG deposits (Omidvar et al., 2022; Sultana et al., 2024a).

Several studies have identified Ca^{2+} as the major metal ion contributing to the formation of FOG deposits and playing a vital role in the proposed mechanism of FOG deposit formation (Yusuf et al., 2023). It is proposed that this is primarily due to the leaching of Ca from cement concrete sewers, a process resulting from the complete dissociation of $\text{Ca}(\text{OH})_2$ into Ca^{2+} and OH^- from concrete (Hu, 2020; Zhang et al., 2023). The dissociation of $\text{Ca}(\text{OH})_2$ is caused either by direct exposure to water or by microbially-induced concrete corrosion (MICC) in sewers, a

phenomenon initiated by sulfur-reducing bacteria (SRB) that produce H_2S (Jiang et al., 2016; Zhang et al., 2023). However, wastewater carrying high FOG loads also contains significant concentrations of other elements such as Mg, Na and K (Gao et al., 2023). The concentrations of these elements in FOG deposits and wastewater vary depending on their sources within the sewerage system. At the point of origin (i.e., kitchen sink and dishwasher), the concentrations of Na (ranging from 75.0 to 717 mg/L) exceed those of Ca (13.6–43.7 mg/L), Mg (2.57–5.97 mg/L) and K (17.2–19.4 mg/L), largely due to the high content of NaOH in dishwashing detergents (Gurd et al., 2019; Williams et al., 2012). In contrast, the concentrations of Ca and Mg in the sewer network are significantly higher, ranging from 4255 to 10940 mg/L and 117–910 mg/L, respectively (Gurd et al., 2019; Sultana et al., 2022; Williams et al., 2012). The sources of Ca^{2+} are primarily from concrete leaching, food, and human and water sources, while Mg^{2+} may originate from water hardness, food and human sources (Ahmad et al., 2022, 2023). The roles of these four common metal ions found in domestic and FSE wastewater in FOG deposit formation are still unknown.

Recent strategies to tackle biocorrosion (Ca leaching), odour and pH in sewers have included the use of $\text{Mg}(\text{OH})_2$ as chemical additives or coating material on the interior surface of the sewers (Cen et al., 2023a, 2023b; Merachtsaki et al., 2020). This approach aims to adjust the pH of the sewer environment to inhibit the activity of SRB and neutralize H_2SO_4 produced from the oxidation of H_2S (Merachtsaki et al., 2020; Zhang et al., 2023). Cen et al. (2023a) conducted a long-term study on the effects of dosing industrial magnesium hydroxide liquid in sewer systems and noted significant alterations in the physicochemical properties of the system. Their research highlighted a considerable accumulation of Mg, reaching 257 mg/L in the effluent. The Birch Bay Water and Sewer District in Western Australia reported an increase in total suspended solids (TSS) in wastewater when using $\text{Mg}(\text{OH})_2$ slurry for odour control and alkalinity maintenance (IER, 2021). They hypothesised that this increase might result from the saponification of Mg^{2+} with diglycerides, forming soaps and dislodging FOG. However, it is possible that these soaps are actually FOG particles that accumulate into deposits. Although this method effectively addresses biocorrosion and controls odour, it might likely promote the accumulation of FOG deposits in the presence of UCO, which remains unclear. Therefore, it is essential to investigate the effect of accumulated Mg^{2+} following $\text{Mg}(\text{OH})_2$ dosing in domestic and FSE wastewater systems, particularly concerning FOG deposit formation in the presence of UCO.

This study focuses on the impact of Mg from $\text{Mg}(\text{OH})_2$ on FOG deposit formation in sewer systems. The emphasis on in-sewer dosing of $\text{Mg}(\text{OH})_2$ is critical, given its recent application in managing odour, pH levels, and biocorrosion. Notably, Sydney Water in Australia has established a standardized specification (SS 211) for using $\text{Mg}(\text{OH})_2$ to control corrosion within sewer systems (Sydney Water, 2024), and Inland Environmental Resources (IER), USA has reported its use in various locations, including South Coast Water District and Pacific Coast, Orange County, USA (IER, 2021). This study seeks to provide critical insights that will contribute to developing proactive and sustainable FOG management practices within the wastewater industry. The specific objectives are to: (a) elucidate the impact of Mg on FOG formation and compare it with the metal ions like Ca, Na, and K commonly found in FOG deposits within sewer systems; and (b) investigate the influence of metal ions, fats/oils (used cooking oil or fresh cooking oil), and FFAs on various aspects of FOG deposits, including

their quantity, physical appearance, FFA profile, metal content, and rheological properties. Understanding the influence of these four metals commonly found in kitchen wastewater is crucial for developing strategies to prevent blockages and mitigate environmental consequences.

2. Material and methods

2.1. Materials

In this study, canola oil sourced from Aldi Supermarket, Australia, was used as the fresh cooking oil (FCO) for the FOG deposition process. To mimic the characteristics of used cooking oil (UCO) typically found in households and FSEs, the UCO was subjected to a deep-frying process with chips and chicken. To assess the impact of elements most commonly found in high concentrations in kitchen wastewater, four metal sources were selected: calcium hydroxide ($\text{Ca}(\text{OH})_2$), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), sodium hydroxide (NaOH), and potassium hydroxide (KOH). As the source of FFA, lauric acid (C12:1), myristic acid (C14:0), palmitic acid (C16:0), stearic acid (C18:0) and oleic acid (C18:1). All chemical were purchased from Sigma-Aldrich Pty Ltd, Australia and used as received. Milli-Q water was used throughout the experiments, and all chemicals were utilised as received without further purification.

2.2. FOG deposition

FOG deposition tests were prepared according to the synthetic wastewater compositions outlined in Table 1. The production of synthetic FOG deposits followed the steps outlined in previous studies (Del Mundo and Sutteerawattananonda, 2017; Kusum et al., 2020) with some modifications. Specifically, synthetic wastewater used for FOG deposition was prepared by mixing 400 mL of Milli-Q water, 40 mL of fats/oils and metal salts (0.1 g/L of each metal ion). The composition of synthetic wastewater was selected to mimic the properties of real restaurant and kitchen wastewater (Ahmad et al., 2023). Additionally, lauric acid, myristic acid, palmitic acid, stearic acid and oleic acid were selected to address the increase in FFA content in the sewer network due to microbial activities in grease interceptors (GIs) and the sewer system. For this experiment, FFAs at 10 mg/mL of UCO were initially mixed with UCO using a magnetic stirrer heated at 60 °C until completely dissolved. After the oil and FFAs were thoroughly mixed, Milli-Q water containing completely dissolved metal salts (0.1 g/L metal ion) was added to the beaker according to the experimental setup outlined in Table 1. All FOG deposition processes were carried out at 450 rpm using a magnetic stirrer for 8 h at room temperature before settling overnight in a 500 mL measuring cylinder. All tests were carried out in triplicate. The apparent volume of FOG deposits produced was measured in the cylinder.

Subsequently, the deposits were recovered from the cylinder for detailed analyses to assess their physicochemical properties.

2.3. Physicochemical properties of FOG deposits

2.3.1. FTIR analysis

Fourier Transform Infrared (FTIR) analysis of FCO, UCO and all FOG deposit samples was recorded using a PerkinElmer Spectrum 100, USA. This qualitative FTIR analysis was used to confirm the presence of saponified solids in the FOG deposits by identifying characteristic bands associated with metal soaps. The detector performed 64 scans over an absorbance spectrum ranging from 400 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1} . Baseline correction and data processing were performed using Originlab ©.

2.3.2. Free fatty acid (FFA) analysis

The FFA profiles of FCO, UCO, UCO + FFA and FOG deposits were determined as fatty acid methyl esters (FAME) following a modified method described by Ahmad et al. (2023). The sample (1 mL for FOG deposit and 1 mL for fats/oils source) was transferred into a vial, 1.5 mL of methanolic NaOH (0.5 M) was added, and the vial was heated in a water bath for 10 min at 85 °C. Then, 1 mL of $\text{BF}_3 \cdot \text{CH}_3\text{OH}$ (14%, wt./vol) was added and heated again at 85 °C for 15 min, after which 3 mL of n-hexane was added and thoroughly mixed. The resulting n-hexane layer was carefully collected and dried under nitrogen gas. Following drying, each sample was solubilised using 1 mL of dichloromethane (DCM) and vortexed for 1 min before transferring into a GC vial for FAME determination via GC-MS with an FID detector (Agilent GC 6890, Agilent Technologies, Australia). Supelco 37 component FAME mix (Sigma Aldrich) in DCM was used as the standard solution.

2.3.3. Metal content analysis

Metal content analysis of FOG deposits was carried out following the method described by Del Mundo and Sutteerawattananonda (2017). Specifically, 1 mL of FOG deposit sample was digested in a thermal glass vial placed in a digestion block (DK 42/26, VELP Scientifica) at 90 °C in a fume cupboard. This process used 10 mL of aqua regia solution ($\text{HCl}:\text{HNO}_3 = 4:1$ vol/vol). After 3 h of digestion, the mixture was allowed to cool before being transferred into a 15 mL tube. It was then centrifuged at 4000 rpm for 15 min and filtered through a 0.45 μm PTFE membrane filter. The filtrate was appropriately diluted and analysed for metal concentrations using Inductively Coupled Plasma-Mass Spectrometry (Agilent 7700 ICP-MS).

2.3.4. Rheological analysis

The rheological properties of the FOG deposits were analysed using a Discovery HR3 Hybrid Rheometer (TA Instruments, USA). Using a TA®

Table 1

Composition of different wastewaters for the production of synthetic FOG deposits (All experiments carried out in triplicate).

FOG deposition process	Fat/oil source		Metal ions				Free Fatty Acids				
	UCO	FCO	Ca	Mg	Na	K	Lauric	Myristic	Palmitic	Stearic	Oleic
1	+		+	+	+	+					
2		+	+	+	+	+					
3	+		+								
4	+			+							
5	+				+						
6	+					+					
7	+		+				+	+	+	+	+
8	+			+			+	+	+	+	+
9	+				+		+	+	+	+	+
10	+					+	+	+	+	+	+
11	+			+			+				
12	+			+				+			
13	+			+					+		
14	+			+						+	
15	+			+							+

plate/plate geometry with a 40 mm diameter and 1 mm gap, the flow behaviour of the samples was assessed across an increasing shear rate range of 0.1–800 s⁻¹ at 25 °C. The instrument directly measured the apparent viscosity of the samples. By employing the Power Law model (Eq. (1)) and identifying the best fitting shear rate range, as outlined by Del Mundo and Sutteerawattananonda (2017), the flow behaviour index (n) and the consistency coefficient (K) were calculated.

$$\tau = K \left(\frac{du}{dy} \right)^n \quad \text{Eq. 1}$$

Where K (Pa.s) is the flow consistency index, $\frac{du}{dy}$ is the shear rate (s⁻¹), and n is the flow behaviour index.

3. Results and discussions

3.1. Formation of FOG deposits

The volumetric measurements used in this study facilitated the determination of the variability of the density and rheology of the FOG deposits. Furthermore, in real-world sewer clogging scenarios, the quantification of volume occupied by FOG deposits determines the magnitude of sewer blockage and potential SSOs. The volume and visual appearance of distinct phases in a measuring cylinder following the FOG deposition process show distinct variations, which were influenced by the composition of the synthetic wastewater (Figs. 1 and 2). Three distinct phases: unreacted excess oil phase, FOG deposit phase and wastewater phase, were observed when Ca, Mg, Na and K underwent a deposition process with UCO (Figs. 1a and 2a). The volume of FOG

deposit was measured as 68.3 ± 2.8 mL. However, only two phases were observed with FCO, with no FOG deposit phase. This finding contradicts the observations of Del Mundo and Sutteerawattananonda (2017), who utilised fresh cooking oil and reported the formation of FOG deposits. In this study, 40 mL of FCO or UCO, representing about 10 wt% of the working volume, was used for the FOG deposit formation process, in contrast to the 74.7 wt% used by Del Mundo and Sutteerawattananonda (2017). Omidvar et al. (2022) also noted a significantly reduced formation of FOG deposits from FCO compared to UCO when using 74.7 wt % of fats/oils sources. The formation of FOG deposits with a high proportion of FCO might be attributed to crystallisation between available FFAs (Gross et al., 2017).

Selected metal ions were individually considered for the FOG deposition process. Three distinct layers were also observed, with Mg producing the highest volume of FOG deposit of 45.0 ± 7.0 mL, followed by Ca (33.5 ± 5.0 mL), Na (26.5 ± 2.1 mL) and K (20.0 ± 2.0 mL). Based on stoichiometry, saponification reactions proceed according to mole ratios. For instance, in the case of Mg, 1 mol of Mg²⁺ reacts with 2 mol of RCOOH to yield 1 mol of Mg(OOCR)₂. Consequently, variations in the atomic masses of the metal ions will impact the generation of FOG deposits. For instance, at a concentration of 0.1 g/L, the molar concentration of Mg²⁺ (0.0041 mol/L) exhibits a higher concentration compared to Ca²⁺ (0.0025 mol/L). Thus, it is likely that more FOG deposits would be formed with Mg than with Ca, as demonstrated in this study, assuming an excess of FFA molecules. Similarly, Na⁺ (0.0043 mol/L) exceeds K⁺ (0.0026 mol/L) at the same metal ion concentration of 0.1 g/L. Divalent metals like Ca and Mg will react with more FFAs compared to monovalent metals such as Na and K. Consequently, the volume of FOG deposits follows the descending order: Mg > Ca > Na >

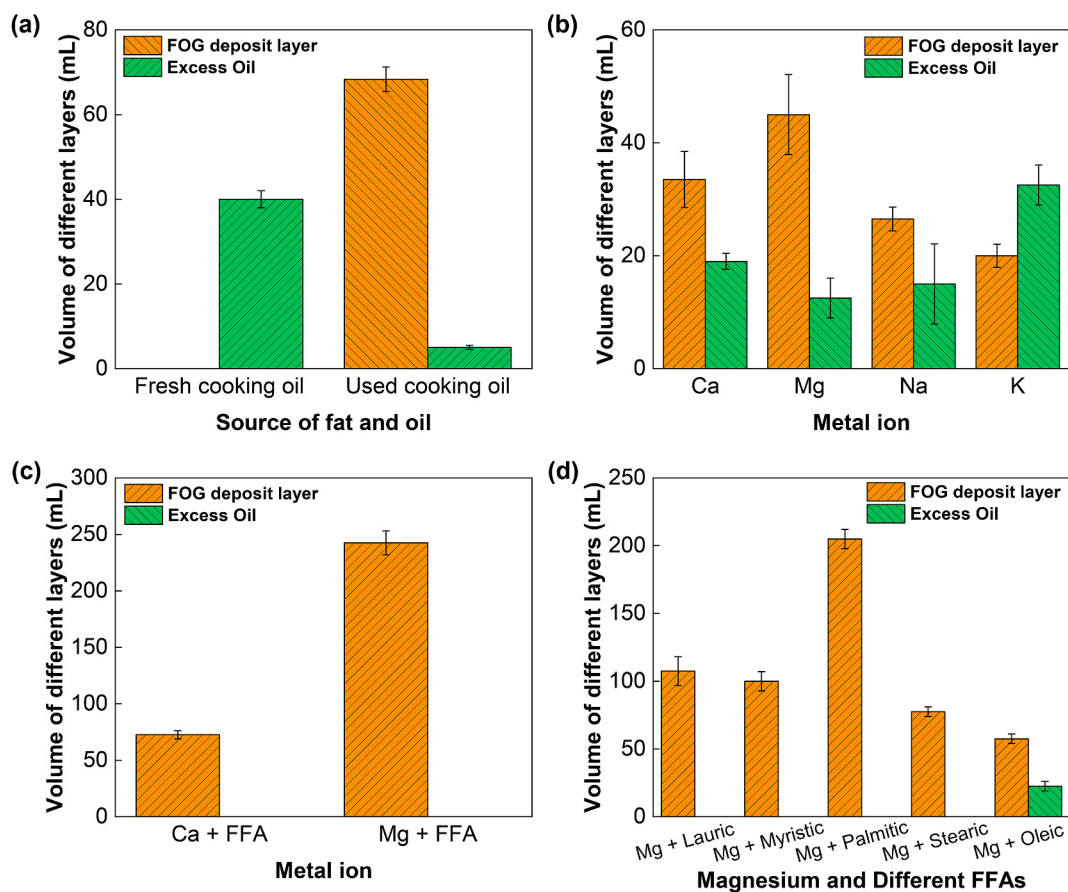


Fig. 1. Volume of different phases after FOG deposit formation under different conditions (a) influence of UCO and FCO and all metal ions (Ca, Mg, Na, and K), (b) influence of different metal ions with UCO, (c) influence of increasing FFAs content by 10 mg/L of each in UCO with different metal ions, (d) influence of increasing different FFA contents by 10 mg/L of each in UCO with Mg.

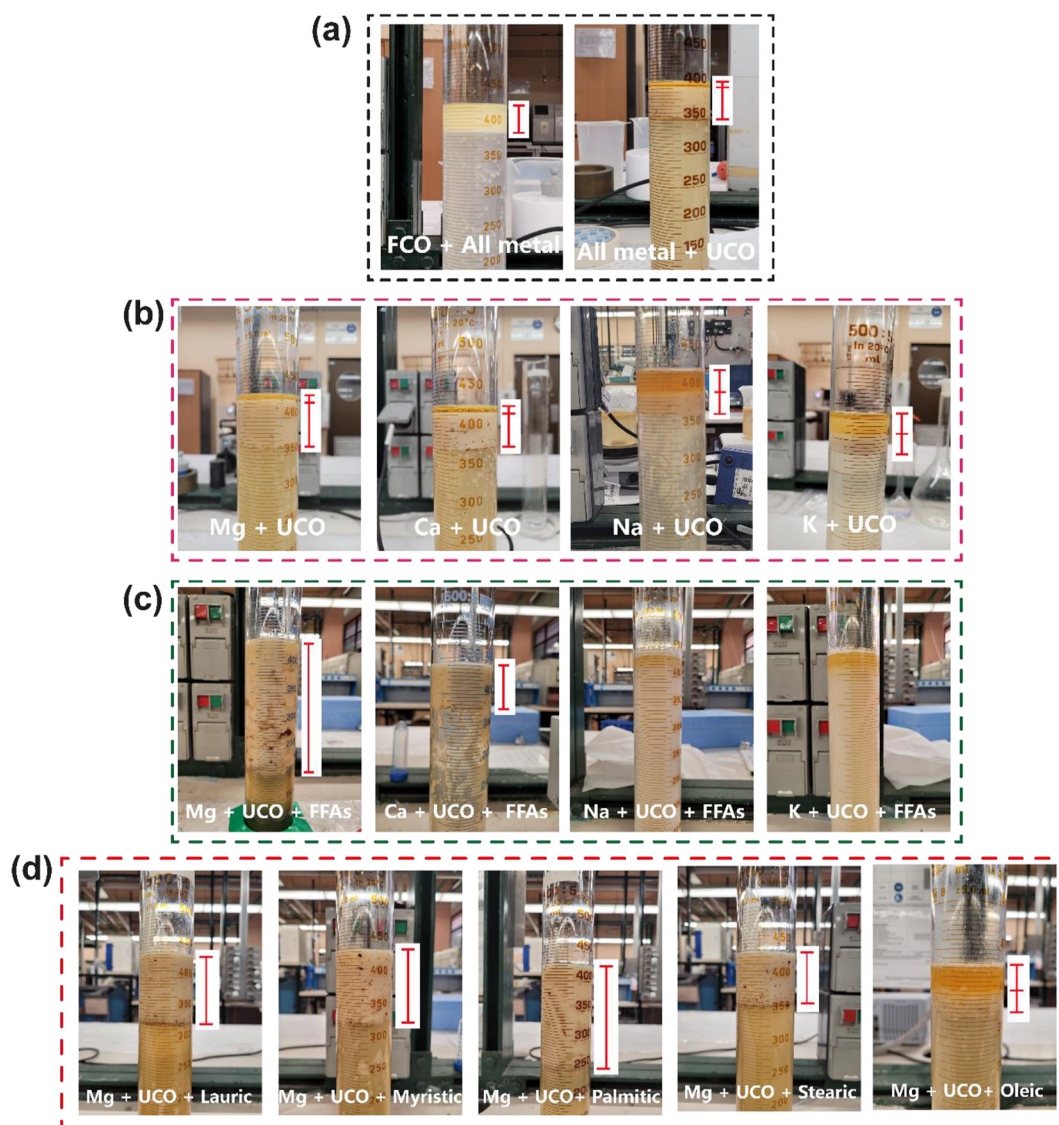


Fig. 2. Separation phases after FOG deposit formation under different conditions (a) influence of all metal ions (Ca, Mg, Na, and K) on FCO and UCO, (b) influence of different metal ions on UCO, (c) influence of increasing FFAs content (10 mg/L of each) in UCO with different metal ions, (d) influence of increasing FFAs content (10 mg/L of each) in UCO with Mg.

K, as depicted in Fig. 2b. In addition, the solubility of these metal ions in water may play a significant role in the aggregation process that leads to FOG deposit formation, with a notable relationship between greater FOG formation and lower solubility product constants of the source metal ions. To ensure a fair comparison of each metal ion's potential to promote FOG deposit formation with UCO, we evaluated the influence of selected metal ions at an equal molar concentration of 0.01 mol/L. The results showed that Mg and Ca produced similar amounts of FOG deposits at 65.5 ± 4.9 mL, while the monovalent ions Na and K resulted in fewer FOG deposits at 40.5 ± 2.0 mL. Additionally, a whitish wastewater layer suggesting the dispersion of FFAs was observed with Na and K rather than the accumulation of FOG deposits (Fig. S1). These findings indicate that Ca and Mg have comparable impacts on FOG deposit formation at the same molar concentrations. However, it is important to note that metal ion concentrations in wastewater are typically reported in mass concentrations rather than molar concentrations. Furthermore, previous studies have primarily implicated Ca in FOG deposit formation, suggesting that in its absence, cooking oil is unlikely to form solid deposits (He et al., 2013). In contrast, our study demonstrates the significant roles of Mg, Na, and K in FOG deposit formation.

To elucidate the influence of increasing FFA concentrations due to microbial activities in the GIs and the sewer system on FOG deposit formation, the FFAs content (lauric, myristic, palmitic, stearic, and oleic acid) was increased by the addition of 10 mg/mL of each to UCO, and the deposition process observed. During the process, yellow-brownish FOG deposit particles were observed for divalent metal ions, with Mg producing larger particles than Ca. After stopping the mixing, the mixture was allowed to settle overnight, after which only two layers were observed: the FOG deposit layer and the wastewater layer. The absence of an unreacted excess oil layer in this process suggests that all available FFAs reacted with Mg and similarly with Ca. The volume of FOG deposit for Mg and Ca used as individual metals was 242.5 ± 10.6 mL and 72.5 ± 3.5 mL, respectively. Aggregation reactions likely contributed to further enhancing the formation of FOG deposits with Mg due to the low solubility of its source ($\text{Mg}(\text{OH})_2$) compared to Ca and its source ($\text{Ca}(\text{OH})_2$).

Interestingly, dispersed particles were observed during FOG deposit formation for UCO with increased FFA content and Na and K as individual metal ions. Neither the FOG deposit layer nor the unreacted excess oil layer was observed. However, FOG deposits were observed between Na or K and UCO (Figs. 1c and 2c). These discrepancies could

be attributed to the bond structure and chemical composition. UCO contains 96% triglycerides, which contain ester bonds between the FAs and glycerol (Mohana et al., 2023). When bases react with triglycerides in UCO, they break the ester bond to form Na FOG deposits, glycerol and unreacted fatty acids (RCOOH). On the other hand, increasing the FFA content in UCO, which already exists in an acidic form with a carboxylic acid group (-COOH), resulted in a dispersed solution, possibly with a high content of unreacted fatty acids with Na and K rather than FOG deposits.

The greater production of Mg and Ca FOG deposits in UCO with additional FFA content was attributed to their higher affinity for the carboxylic acid groups. This increased affinity stems from their charge (divalent) density, which more readily displaces hydrogen ions from the carboxylic acid groups. To further elucidate the FOG deposition potential of magnesium ions, different fatty acids were investigated for FOG deposit formation with Mg as metal ion (Figs. 1d and 2d). Mg and palmitic acid produced the largest volume of FOG deposit at 205.5 ± 7.0 mL. In comparison, lauric, myristic acid and stearic acid produced 107.5 ± 10.6 mL, 101.3 ± 7.0 mL and 77.5 ± 3.5 mL of FOG deposit, respectively. However, the addition of oleic acid led to three distinct phases: unreacted excess oil, FOG deposit (57.5 ± 3.5 mL) and wastewater. The presence of unreacted oil with oleic acid, compared to the other FFAs, is linked to its chemical structure, which contains cis double bonds in its carbon chain, creating a kink or bend which prevents the FFA molecules from packing tightly together. The saturated FFAs exhibit a greater contribution to the formation of FOG deposits, as evidenced in this study, attributable to their linear molecular structure enabling tighter packing. Supporting evidence is provided by Gross et al. (2017) who observed higher yield strength in FOG deposits with palmitic acid

compared to other FFAs.

The major FFA found in real FOG deposit samples is predominantly palmitic acid, which is present in concentrations of about 70 mg/g of FOG deposits (He et al., 2013; Williams et al., 2012). Recently, Ahmad et al. (2023) also found a high proportion (41%) of palmitic acid in restaurant wastewater, along with other FFAs such as linoleic acid (polyunsaturated) and oleic acid (monounsaturated). Williams et al. (2012) further suggested the possible transformation of oleic acid to palmitic through the β -oxidation mechanism by microorganisms within the GIs and the sewer networks. These findings indicate that FOG deposit formation in sewers is likely to persist as the production of FFAs, especially palmitic acid, increases in GIs and sewer networks.

3.2. Free fatty acids profile

Linoleic acid (C18:2), a polyunsaturated fatty acid, constitute the largest proportion of fatty acids in FCO at 40.41%, followed by oleic acid and α -linoleic acid at 26.54% and 22.16%, respectively. In contrast, UCO exhibited higher oleic (C18:1) acid (53.73%) and lower linoleic (C18:2) acid (24.91%) and α -linoleic acid (13.7%) content. The decrease in the proportion of linoleic acid and α -linoleic acid compared to FCO was attributed to the conversion of polyunsaturated and unsaturated fatty acids to saturated fatty acids (Omidvar et al., 2022). In addition, the transfer of fatty acids from the food items (chicken and chips) during frying is suggested to contribute to the increased saturated fatty acid content (Sultana et al., 2024b; Williams et al., 2012). Notably, the FFA composition of different FOG deposits mirrors that of their respective fat and oil sources (Fig. 3b and c).

Understanding the percentage distribution of FFAs in FOG deposits

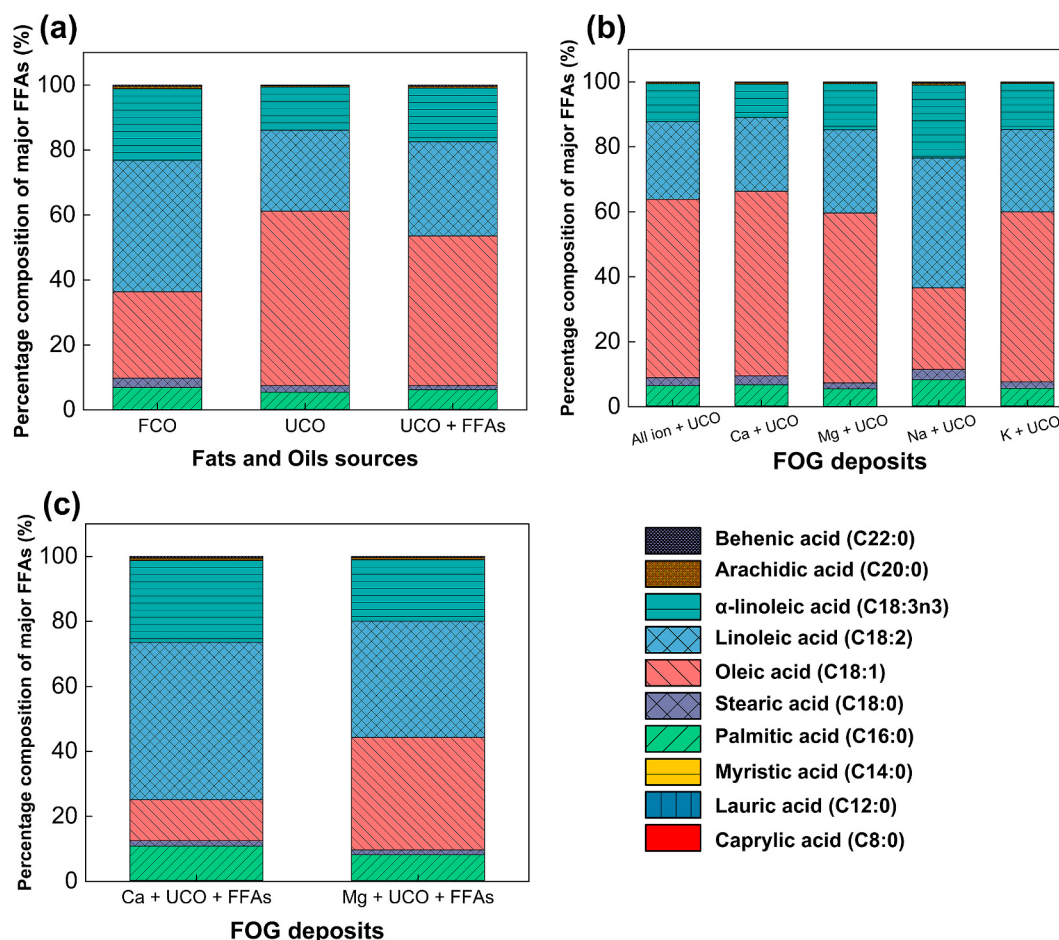


Fig. 3. FFAs composition in FCO, UCO and FFA amended UCO and the resultant FOG deposits.

with various metal ions is important to elucidate their roles in the formation process (Fig. 4). The distribution of FFAs, as shown in Fig. 4a, closely relates to the FFAs profile in UCO (Fig. 3a). The proportion of total FFAs contributing to FOG deposit formation was higher in Mg FOG deposits at 69.5%, followed by Ca, Na and K FOG deposits with percentages of 57.8%, 34.6% and 21.7%, respectively (Fig. 4a). Saturated FFAs accounted for the largest percentage involved in the FOG deposit formation compared to unsaturated FFAs. Of these saturated FFAs, stearic acid and palmitic acid were the most FFAs involved in Mg (81.9% and 73.0%, respectively) and Ca (87.5% and 71.2%, respectively). These findings align with the amount of FOG deposits produced, as shown in Fig. 1b.

Increasing FFAs content for FOG deposit formation potentially increased the availability of FFAs molecules to undergo reaction with metal ions. This is evident as the total FFAs in the FOG deposits after formation compared to the fats/oils source increased to 74.8% with Mg and 59.6% with Ca (Fig. 4b). Moreover, saturated FFAs added, as well as those present in the UCO, contributed to FOG deposit formation. The percentage of saturated FFAs transferred into Mg-FOG deposits and Ca-FOG deposits with increased FFAs content was 95.1% and 92.7%, respectively. This shows that straight-chain saturated FFAs with shorter chain lengths and more molecules in the system compared with the longer-chain unsaturated FFAs are more likely to influence FOG deposit formation in sewer systems. Palmitic, lauric and myristic acid contributed to FOG deposit formation for both Mg and Ca. However, stearic acid indicated a higher contribution to Mg FOG deposits at 95.3% than Ca FOG deposits at 78.9%. In addition, added unsaturated FFA (oleic acids) also showed a higher distribution in Mg FOG deposits (56.3%)

than Ca FOG deposits (15.5%). This explains the high production of FOG deposits with Mg (Fig. 1c) than Ca, suggesting aggregation reaction and the availability of additional FFAs as the contributors to enhanced FOG deposition.

The composition of FFAs in FOG deposits in this study aligns with the FFA profiles found in FOG deposits from previous studies and field samples (He et al., 2013; Williams et al., 2012). These findings underscore that both the source and the type of FFAs play pivotal roles in the formation of FOG deposits. Moreover, the use of UCO provides valuable insights into the underlying mechanisms of FOG formation, reinforcing the observations made by Omidvar et al. (2022).

3.3. FTIR analysis

FTIR analysis was performed on cooking oil samples before and after deep-frying to provide evidence of changes during the process. Fig. 5a shows the spectra of FCO and UCO, with characteristic bands similar to those reported in previous studies, with peaks observed around frequencies of 1350 cm^{-1} , 1745 cm^{-1} and 2925 cm^{-1} , with variations in their intensities reflecting changes in the content of saturated and unsaturated FFAs (Kaur et al., 2019; Omidvar et al., 2022). The peak absorbance around 1745 and 2925 cm^{-1} for UCO appears higher than that of FCO. This is linked to the production of polar functional groups, such as ester, aldehyde and ketone, ascribed to the peak at 1745 cm^{-1} , which are reported to increase due to oxidative degradation after cooking (Choe and Min, 2007; Omidvar et al., 2022).

As previously highlighted, the mechanism of FOG deposit formation is primarily attributed to the saponification reaction between FFAs and metal ions. Hence, the disappearance of the carbonyl band at 1745 cm^{-1} and the appearance of a band around 670 cm^{-1} and a broad band around 3400 cm^{-1} are associated with metal soap formation (He et al., 2011; Iasmin et al., 2014). Fig. 5b–d presents the FTIR analysis of the different FOG deposits. The semi-solids produced from UCO with various metal ions were confirmed as FOG deposits based on the FTIR analysis (Fig. 5b), showing similarities to FOG collected from a residential kitchen and an apartment (He et al., 2013). These changes in the spectra indicate the formation of FOG deposits, as reported previously using a similar concept by Omidvar et al. (2022). Moreover, the spectrum of the unreacted oil collected from the FCO FOG deposition process did not resemble those of FOG deposits.

The relative absorbance intensity around 1745 cm^{-1} for Ca and Mg is significantly lower than that of Na and K (Fig. 5c and Table S1). This suggests that compared to the relative peak intensity in UCO, a greater proportion of FFAs reacted with Mg and Ca than Na and K, which had a higher content of unreacted FFAs. Similarly, when the FFA content in UCO was increased, the relative absorbance intensity around the 1745 cm^{-1} bands increased, and following FOG deposition with Ca, Mg, Na and K, this intensity decreased (Fig. 5d and Table S1). The notable differences in absorbance intensity among the metal ions is attributed to their molar concentration and valency, as highlighted previously. Furthermore, the metal – oxygen absorption band intensity around 670 cm^{-1} is associated with the strength of bonds and the formation of FOG deposits. The higher the absorption intensity of the band, the greater the content of metal ions in the FOG deposits (Del Mundo and Suthewarawattananonda, 2017; Poulenat et al., 2003). The relative absorbance intensity of the Mg–O bond (around 670 cm^{-1}) was stronger than those of the Ca–O, Na–O and K–O bond. This aligns with the decrease in absorbance at the 1745 cm^{-1} band, which further demonstrates that saponification and aggregation reactions occurred during the formation of FOG deposits.

3.4. Metal analysis

The proportion of metal ions in various phases following the FOG deposition process was analysed (Fig. 6a–d). In the FOG deposition process containing all four metal ions, the proportion of Mg in FOG

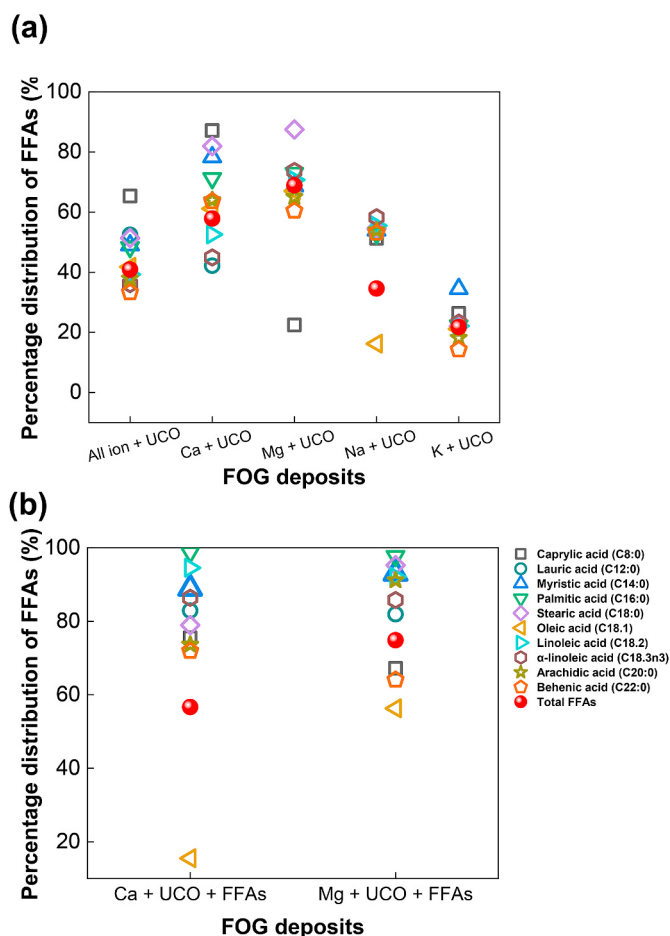


Fig. 4. Percentage distribution of FFAs in FOG deposits compared to their corresponding fats and oil sources.

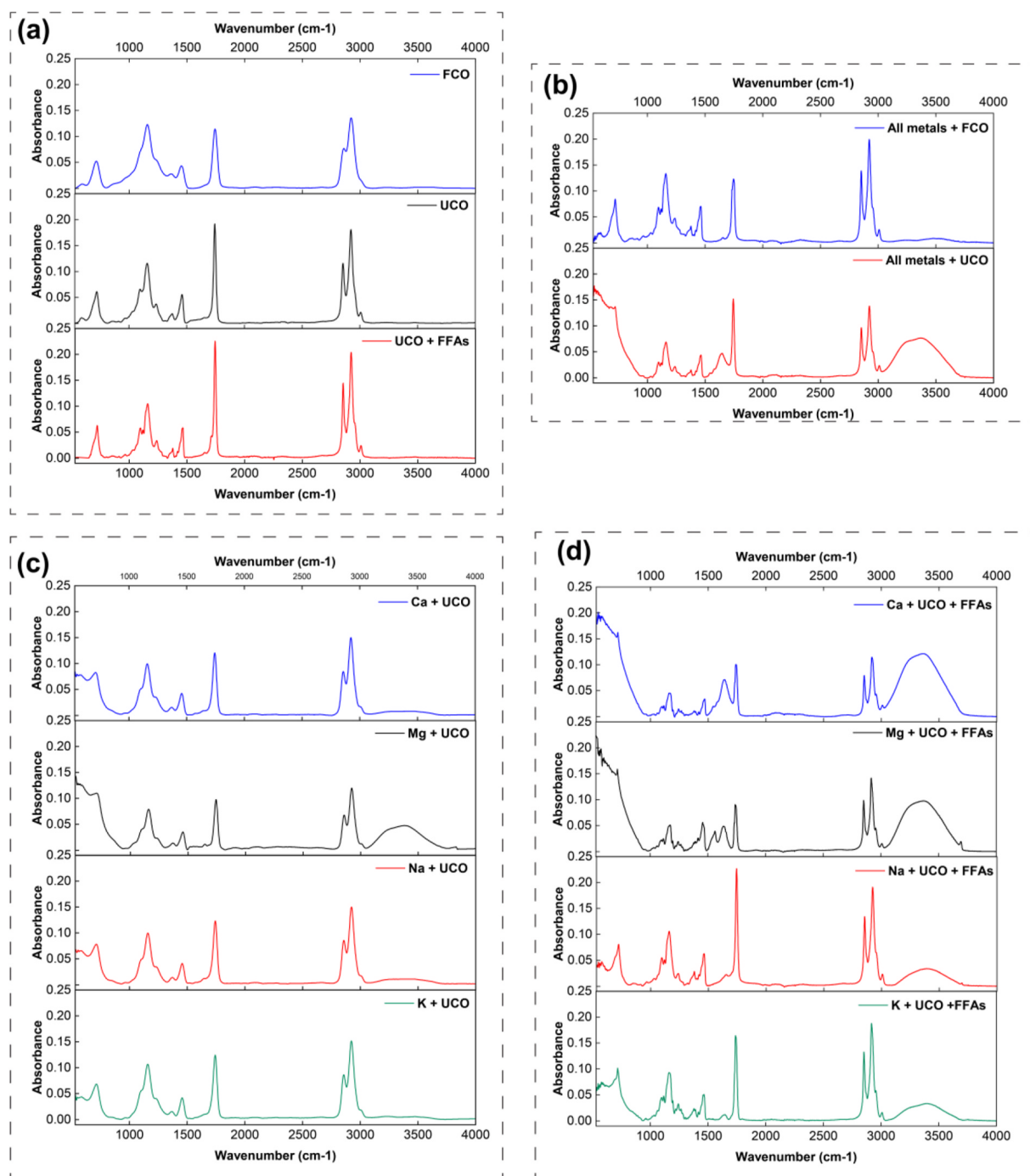


Fig. 5. FTIR spectra of FCO and UCO and FOG deposits prepared under different conditions (a) FCO, and UCO with and without added FFAs, (b) FCO and UCO FOG deposits with all metal ions (Ca, Mg, Na, and K), (c) UCO FOG deposits with different metal ion content (d) UCO FOG deposits with added FFAs content with different metal ions.

deposits was 72.3% of the added metal ion concentration, which is significantly higher than the proportion of Ca (14.9%), Na (5.6%) and K (7.2%) (Fig. 6a). Stoichiometrically, saponification reactions should occur between FFAs and divalent metals at a molar ratio of 2:1 and between FFAs and monovalent metals at a ratio of 1:1 (Williams et al., 2012). This suggests that divalent metals are more likely to produce a greater quantity of FOG deposits during saponification reactions, as shown in Fig. 6a. Compared to Ca, the high proportion of Mg in FOG deposits might result from the attraction of excess metal ions towards the FOG matrix, as explained by the DLVO theory (He et al., 2013). In addition, the solubility product constant (K_{sp}) of metal ions influences

the aggregation reaction. This is evident as $Mg(OH)_2$ ($K_{sp} 1.38 \times 10^{-11}$) is less soluble in water compared to $Ca(OH)_2$ ($K_{sp} 6.5 \times 10^{-6}$) (Ziegenheim et al., 2020). Moreover, a higher proportion of Na and K were detected in the water layer, suggesting that the solubility of metal ions plays a crucial role in the FOG deposition process (Mohana et al., 2023).

In the FOG deposition process using single metal ions, 87.6% of Mg was found in the Mg-FOG deposit. In comparison, only 57.6%, 28.6% and 33.8% of Ca, Na and K, respectively, were detected in their respective FOG deposits. This suggests that the lower the solubility of the metal ion, the greater the production of FOG deposit (Fig. 6b). When the FFA content in UCO was increased for the FOG deposition process, a

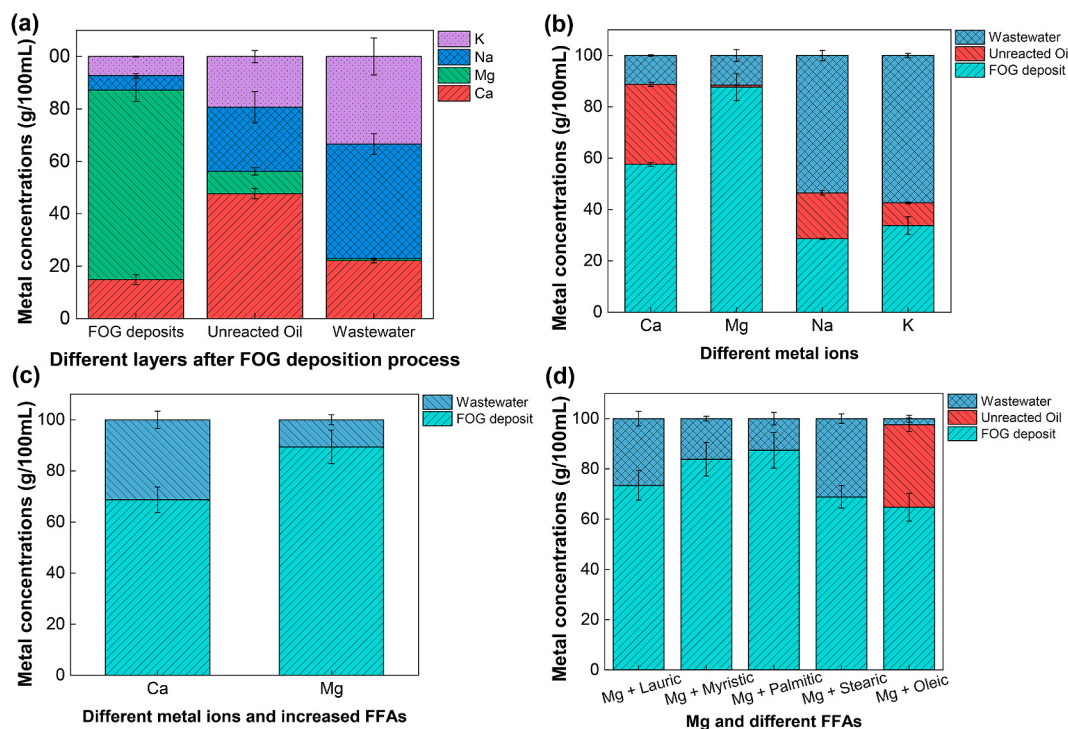


Fig. 6. Proportion of metal concentration added in different phases after FOG deposit formation with (a) UCO and all metal ions, (b) different metal ions with UCO, (c) increased FFAs content in UCO with different metal ions, (d) increased different FFAs in UCO with magnesium.

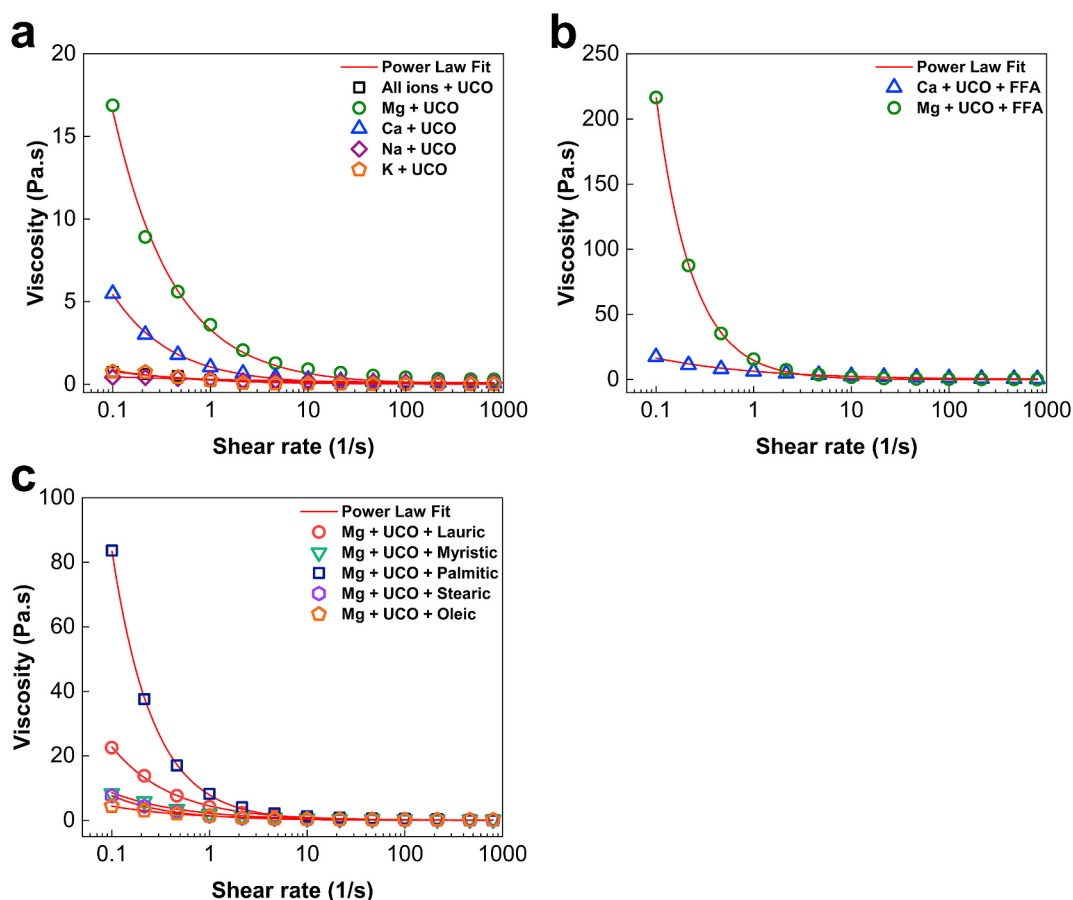


Fig. 7. Rheological analysis and Power Law fitting of FOG deposits.

similar pattern of metal distribution was observed (Fig. 6c), with 89.4% of Mg detected in the FOG deposits compared to 68.7% of Ca, which could also be linked to the solubility constant (K_{sp}) of these metals. Furthermore, the distribution of Mg in different phases after FOG deposition with various FFAs was investigated (Fig. 6d). The proportion of Mg in the FOG deposits of UCO with different FFAs correlated with the amount of FOG deposit produced. For instance, Mg + palmitic acid FOG deposits had the highest Mg proportion of 87.4% compared to other Mg + saturated FFAs. In contrast, the distribution of Mg in the three layers of Mg + oleic (an unsaturated FFA) showed 32.9%, 64.7% and 2.4% in the unreacted excess oil phase, FOG deposit phase and wastewater phase, respectively. The high proportion of Mg in the unreacted oil phase demonstrates that the *cis* double bond in oleic acid limits its interaction with Mg ions.

These findings confirm that a larger amount of Mg from $Mg(OH)_2$ undergoes saponification and aggregation reactions compared to Ca from $Ca(OH)_2$, resulting in the formation of larger and more viscous FOG deposits. This is further supported by the rheological analysis presented in Section 3.5.

3.5. Rheological analysis

Fig. 7 presents the rheological analysis of various FOG deposits generated in this study. A noticeable trend was the gradual decrease in the apparent viscosity as the shear rate increased from 0.1 to 800 s^{-1} at 25 °C. As shown in Fig. 7a, FOG deposits containing Mg, Ca, Na and K exhibited an initial apparent viscosity of 0.78 Pa s at 0.1 s^{-1} , which diminished with increasing shear rates. It is important to recognise that the viscosity of FOG deposits is heavily influenced by several factors, including the profiles and concentrations of FFAs, metal ion content, and water content (Del Mundo and Sutteerawattananonda, 2017). Notably, the type of metal ion and the type of FFA exerted a significant influence on the rheological characteristics of the FOG deposits (Fig. 7a and c).

At an initial shear rate of 0.1 s^{-1} , the apparent viscosities of FOG deposits from Mg, Ca, Na and K were 16.88 Pa s, 5.49 Pa s, 0.42 Pa s and 0.75 Pa s, respectively. The divalent metal ions led to obviously higher apparent viscosity compared to the monovalent ones, which is attributed to greater saponification and aggregation as evidenced by the volume of FOG deposit produced (Fig. 1). There was a significant increase in apparent viscosity, particularly for Mg, when the FFA content was increased for FOG deposit formation with Mg and Ca individually. Specifically, the viscosities increased to 216.50 Pa s for Mg and 17.32 Pa s for Ca FOG deposits at the same initial shear rate of 0.1 s^{-1} (Fig. 5b). Furthermore, the viscosity of FOG deposits with different added FFAs with Mg showed variations. Palmitic acid displayed the highest apparent viscosity of 83.57 Pa s at an initial shear rate of 0.1 s^{-1} followed by lauric (22.51 Pa s), myristic (8.39 Pa s), stearic (7.58 Pa s) and oleic acid (4.36 Pa s) (Fig. 5c). Omidvar et al. (2022) also observed a higher apparent viscosity in UCO containing a high content compared with a lower palmitic content. Similarly, Gross et al. (2017) demonstrated increased strength of FOG deposits with increased concentrations of palmitic acid, whereas it diminished with increasing levels of oleic acid. These results align with the outcomes of the current study, underscoring the significant impact of specific FFAs, particularly palmitic acid, on the rheological properties of FOG deposits.

The Power Law model was employed to simulate the experimental rheological analysis (Fig. 7), and Table 2 shows the derived fitted parameters, consisting of the consistency index (K), flow behaviour index (n) and R^2 value. The flow index represents the changes in viscosity with increasing shear rates (Irgens, 2013). As shown in Table 2, the negative flow behaviour index suggests that the FOG deposits exhibited shear-thinning behaviour, characteristic of non-Newtonian fluids (Goodrum et al., 2003; Irgens, 2013). This non-Newtonian behaviour of FOG deposits is consistent with findings by Iasmin et al. (2014) and Del Mundo and Sutteerawattananonda (2017). On the other hand, the consistency index reflects the resistance of FOG deposits to deformation

Table 2

Power Law parameters of FOG deposits.

FOG deposits	Power Law parameters		
	Consistency index (K)	Flow behaviour index (n)	R^2 value
	(Pa.s)	1/s	
All ions + UCO	0.283	−0.442	0.95
Mg + UCO	3.304	−0.699	0.99
Ca + UCO	1.045	−0.715	0.99
Na + UCO	0.295	−0.183	0.96
K + UCO	0.246	−0.538	0.94
Ca + UCO + FFAs	6.365	−0.414	0.99
Mg + UCO + FFAs	14.648	−1.17	0.99
Mg + UCO + Oleic	1.349	−0.512	0.99
Mg + UCO + Palmitic	7.846	−1.027	0.99
Mg + UCO + Lauric	4.468	−0.706	0.99
Mg + UCO + Stearic	1.413	−0.731	0.99
Mg + UCO + Myristic	2.223	−0.584	0.99

under increasing shear rates (Goodrum et al., 2002). A higher consistency index indicates a greater resistance of FOG deposits to flow, which is particularly relevant in sewer systems (Irgens, 2013). The consistency indexes for all Mg ion-related FOG deposits showed an R^2 value greater than 0.99 and a significantly high consistency index. In contrast, the monovalent ion (Na and K) FOG deposits had an R^2 value below 0.96 and a significantly low consistency index below 1. This suggests that the Mg and Ca FOG deposits have a higher potential to impede flow within the sewer, potentially leading to blockages and subsequent SSOs compared to Na and K FOG deposits.

4. Implications and future research perspective

This study elucidates the role of Mg ions in the FOG deposition process with UCO and the roles of other metal ions, such as Ca, Na, and K, which are found in high concentrations in wastewater. Our findings reveal that Mg^{2+} from $Mg(OH)_2$ significantly enhances the formation of FOG deposits through saponification reactions with FFA. FOG deposits formed with increased FFAs content in the presence of Mg were highly viscous and exhibited a notably high consistency index, indicating a substantial resistance to flow within sewer networks. Among the various FFAs, palmitic acid was observed to produce the largest amount of FOG deposit. These findings provide insight into the active role of $Mg(OH)_2$ on FOG deposit formation from FFAs present in UCO. This suggests that the use of $Mg(OH)_2$ for biocorrosion should be applied with caution as they could cause unintended FOG deposit formation and SSOs. However, further studies are required to investigate the optimal concentration of $Mg(OH)_2$ dosage without substantial adverse effects (FOG formation). The observed effect of Mg^{2+} was with $Mg(OH)_2$, and this phenomenon might not be similar to Mg^{2+} in wastewater from other sources, such as $MgCO_3$ and $MgCl_2$. Future work should investigate the role of Mg^{2+} from different sources, as well as pH effects. In addition, lab-scale pipe loop studies could be employed to monitor the accumulation and growth rate of FOG deposits over time in response to in-sewer $Mg(OH)_2$ dosing, thereby contributing to the development of more refined strategies for mitigating biocorrosion and FOG deposit formation in sewer networks.

5. Conclusions

This research elucidated the impact of used cooking oil (UCO) and metal ions (Ca, Mg, Na and K) on the formation of FOG deposits within sewer systems, with a particular focus on the pronounced role of Mg^{2+} from magnesium hydroxide ($Mg(OH)_2$) used to counteract calcium leaching (Ca^{2+} from $Ca(OH)_2$). Mg^{2+} was identified as the most significant contributor to the formation of highly viscous FOG deposits, which

presents a substantial risk of sewer clogging. The interaction between Mg and FFAs, particularly through saponification and aggregation reactions, leads to these dense deposits. Notably, the saturated FFA palmitic acid, which is predominantly present in various fats and oil sources and found in high concentrations in GIs and within sewer networks due to microbial activities, leads to the production of substantial volumes of FOG deposit on reacting with Mg. These deposits are characterised by their high apparent viscosity and consistency index, posing a significant risk of impeding flow within the sewer network, potentially leading to blockages and SSOs. On the other hand, Na and K ions were found to produce smaller quantities of FOG deposits. Moreover, on increasing the FFA content of the UCO, these ions tended to form dispersed particles rather than dense deposits, leading to FOG deposits with low apparent viscosity and a consistency index (*K*) of less than 1. This indicates that deposits formed in the presence of Na and K are less likely to contribute to sewer blockages, even at reduced flow rates. The insights gained from this research shed light on the complex dynamics of FOG deposit formation in sewer networks and underscore the need for developing more effective and sustainable strategies for managing FOG and MICC.

CRedit authorship contribution statement

Hamza Hassan Yusuf: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Felicity Roddick:** Writing – review & editing, Visualization, Resources, Project administration, Conceptualization. **Veeriah Jegatheesan:** Writing – review & editing, Supervision. **Bruce Jefferson:** Writing – review & editing, Conceptualization. **Li Gao:** Writing – review & editing, Supervision, Resources. **Biplob Kumar Pramanik:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Conceptualization.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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Uncovering the impact of metals on the formation and physicochemical properties of fat, oil and grease deposits in the sewer system

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