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Review

Application of Phase-Selective Organogelators (PSOGs) for Marine Oil Spill Remediation

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Abstract: Oil spill incidents frequently cause serious impacts on the ecosystem, society, and economy. To cope with this problem, the use of phase-selective organogelators (PSOGs) has been developed in recent years as a promising oil spill response tool, which can congeal oils from biphasic systems, accelerating oil removal and recovery and reducing impacts on the environment. This article systematically reviews reported technologies for the use of PSOGs for potential oil spill remediation in the literature from January 2016 to May 2022. It discusses several kinds of PSOGs based on molecular structures which are possible for gelling oil in the presence of water/seawater. Their mechanisms for phase-selective gelation are summarized, including hydrogen bonding, π–π stacking interactions, van der Waals force, hydrophobic interactions, etc. The currently possible deployment methods for the application of PSOGs are explored; carrier solvents and powder form are frequently used. Moreover, the challenges and the corresponding recommendations regarding standardized testing protocols and evaluation framework, gelation selectivity, as well as challenges in field tests, are further discussed.

Keywords: oil spill response; phase-selective organogelators; chemical treatment; solidifiers; oil recovery; oil-water separation

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1. Introduction

Spilled oil from oil extraction and transportation activities is an important source of marine pollution, which results in serious consequences to the ecosystem, society, and human health [1]. To solve this problem, a wide range of oil spill response techniques are deployed to control oil spills and minimize their detrimental impacts [2,3]. Typically, the response methods can be categorized into physical (water washing, sorbent, and raking and bulldozing), mechanical recovery (booms and skimmers), chemical treatment (dispersants, surface washing agents, and solidifiers), and biological methods (adding nutrients or microorganisms) [4,5]. These techniques are affected by various factors including the types and size of the oil spill, the tide and wave strength, meteorological conditions, and logistical constraints, while their fast and effective application can significantly reduce the damage to the affected areas [6–8].

Traditional oil spill response strategies always have some limitations in terms of their actual application [9,10]. The use of booms for example, is restricted by weather and oceanographic conditions and it is usually only feasible for treating spilled oil with high viscosity [11–13]. Chemical treatment might be a good choice for oil spill remediation, while some agents, such as dispersants and surface washing agents, are chemically synthesized and may have certain toxicity to the aquatic systems [14,15]. The use of solidifiers is a feasible option for oil spill response as they can change the physical state of the oil from a liquid to a semi-solid or solid, which can be easily removed and recovered from

the environment [2,16]. An efficient solidifier can solidify the spilled oil rapidly at a low solidifier-to-oil ratio. In recent years, the phase-selective organogelators (PSOGs) have emerged as one type of solidifier to selectively congeal oil from biphasic systems [17,18]. The PSOGs can achieve selective partitioning of the oil phase from the biphasic mixture, and then self-assemble into a network structure for oil gelation through supramolecular interaction. They have been proven to be a promising approach for marine oil spill response due to the advantages of gelation with oils, easy oil separation and recovery, and biocompatibility [19]. In the gelation test for oil/water mixtures, the PSOG molecules go through a supramolecular assembly, fibril structure, and 3D network structure in turn to the supramolecular organogels within the oil phase to encapsulate spilled oil [20].

Research on PSOGs has made significant advances in marine oil spill remediation, and a series of previously critical problems are gradually being solved [21–23]. To facilitate the uniform dispersion of PSOGs in the oil layer, the water-miscible or immiscible carrier solvents are introduced into PSOGs to achieve effective gelation [17,24]. Moreover, powder PSOGs can directly be applied on the oil phase without carrier solvents. This can avoid threats to the marine systems [25]. Even though co-solvents are involved in the deployment of PSOGs, they can be congealed with the oil and PSOGs for further treatment and will not enter into the environment [26]. The PSOGs are considered as a promising oil spill response option, but they are not currently commercially available, because some knowledge gaps still exist, including the complex synthesized process, effects in large-scale deployment, effects of gelation oils without selectivity, and a lack of application guidelines [27].

The objective of this review is, therefore, to comprehensively review recent PSOG technologies for marine oil spill remediation published in the period of January 2016 to May 2022. It will discuss several kinds of PSOGs, based on molecular structures, that are possible for gelling oil in the presence of water or seawater, and mechanisms for phase-selective gelation will be summarized. The current possible deployment methods for the application of PSOGs in real scenarios will be introduced. Moreover, challenges in the development of this technique for oil spill response will be identified and recommendations for future research will also be provided.

2. PSOGs for Oil Spill Response

2.1. General Description of PSOGs

As one subclass of low molecular weight organogels (LMWGs), PSOGs are able to congeal organic phases such as oils in the presence of water, and they thus have great potential for oil spill response and recovery (Figure 1) [28]. The gels are physically formed, driven by noncovalent intermolecular interactions such as hydrogen bonding, π–π stacking, and van der Waals interactions, and their xerogel forms usually show the formation of the fibrous entangled morphologies, further assembling into 3D porous network structures [29,30]. The congealed oil by PSOGs has excellent physical and thermal stability, so it can be easily collected from the water surface by mechanical methods such as filtration and skimming, reducing potential adverse impacts to the environment [31,32]. Meanwhile, the oil and PSOGs can be separated and recovered from the collected gels for further recycling. For example, diesel oil can be obtained using the vacuum distillation method [26,33]. Compared with conventional methods, PSOGs have some advantages in treatment of spilled oil. First, PSOGs can gel the oil slick on an open water surface to limit the oil spreading to coastal environments and improve the efficiency of mechanical removal [16,34]. Second, the breakup and dispersion of the oil can be constrained and delayed by PSOGs due to the cohesive force of the formed gel, so the time window for effective response will be extended [27]. Moreover, unlike most oil spill treatments, the deployment of PSOGs may not be restricted by rough seas and meteorological conditions. Therefore, PSOGs can be a promising candidate for marine oil spill remediation.

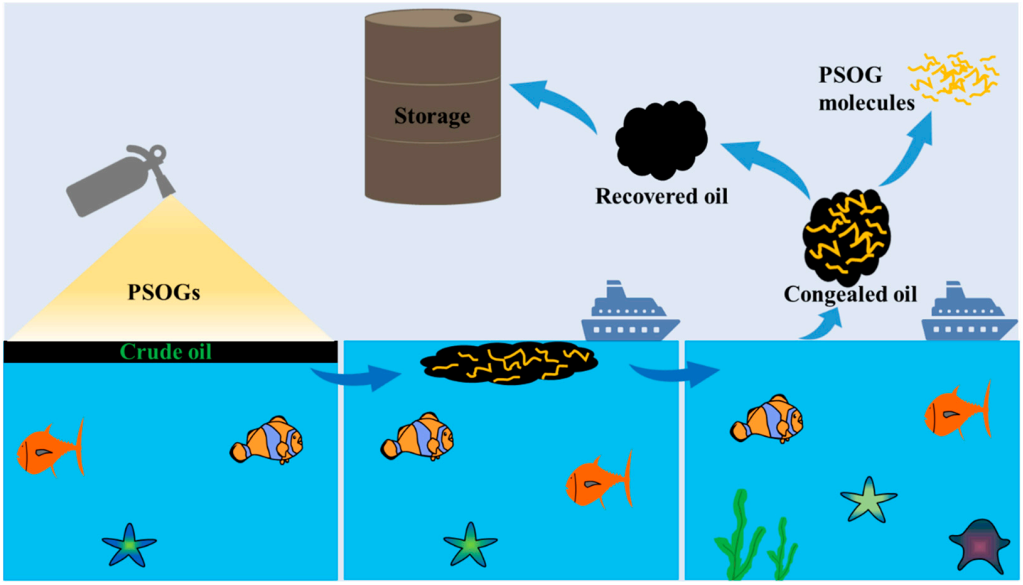


Figure 1. Potential application of PSOGs in oil spill response and recovery.

According to existing literature, an ideal PSOG is required to address the following problems to be applicable to real-world scenarios: (i) selective and efficient gelation with spilled oil without carrier solvents or heating/cooling processes; (ii) easy and low-cost synthesis; (iii) environmentally friendly nature and mechanical stability; (iv) recoverability and recyclability [35,36]. For the past few years, various PSOGs have been developed to satisfy some of the above requirements in marine oil spill responses. They can be divided into several categories based on their molecular structures, including amino acid/peptide-based PSOGs, sugar-based PSOGs, amide derivatives, organic salts, and cholesterol derivatives.

2.2. Amino Acid/Peptide-Based PSOGs

The PSOGs derived from amino acids or peptides have been widely studied due to their nanofibrous structure that is like collagen, good biocompatibility, strong molecular designability, and sensitive response to external field stimuli [28,37,38]. The first reported PSOGs for water-oil separation, proposed by Bhattacharya and Krishnan-Ghosh [39], were also based on amino acid derivatives. They demonstrated a promising way to combat oil pollution problems. Even in recent years, there have been many studies which focused on amino acid or peptide-based PSOGs for oil spill recovery [38,40–42]. Ren et al. [43] synthesized a series of PSOGs from fluorenylmethoxycarbonyl (Fmoc)-protected amino acids, which were low-cost and low-toxic for the gelation of crude oil with different densities and viscosities. Notably, two of them were able to congeal one light crude oil in the powder form, while the gelation time was seen to be up to 48 h. Later, Ren and co-workers [44] systematically investigated 48 PSOGs with monopeptide-based structures and found that two of the best-performing PSOGs could not only congeal four kinds of oils but also have at least three times lower costs than their counterparts with Fmoc groups.

A dipeptide-based amphiphilic PSOG **1** was also developed and evaluated for the gelling of refinery products, crude oil, and diesel in the presence of water. Experiments exploring the effects of the crude composition on gelling ability were performed with crudes of varying APIs, from 18.7 to 40.5 (Figure 2) [45]. Podder and his co-workers [46] synthesized a set of tripeptide-based PSOGs **2**–**5** with different steric crowding in the central amino acid residue. The results revealed that only PSOGs **2** and **4**, which were less sterically hindered, can gel saturated hydrocarbons, crude oil, and aromatic solvents from biphasic mixtures at room temperature. In the same year, Zhang et al. [32] also reported a series of PSOGs **6**–**8** synthesized by Fmoc-L-serine and amines with different lengths of alky chains, and they found that the gelation time increased significantly from 1 s to 2 h with

the increase of the alkyl chain length (Figure 2). That might be attributed to the fact that the PSOG with a shorter alkyl chain needs less time to reach stable self-assembly due to the relatively simple van der Waals interactions between PSOG and the solvent. Meanwhile, the mechanical strength of the PSOGs was also explored by the measurement of oscillation frequency and dynamic oscillatory stress, and the results indicated that PSOGs with shorter carbon chains had excellent stiffness and mechanical strength.

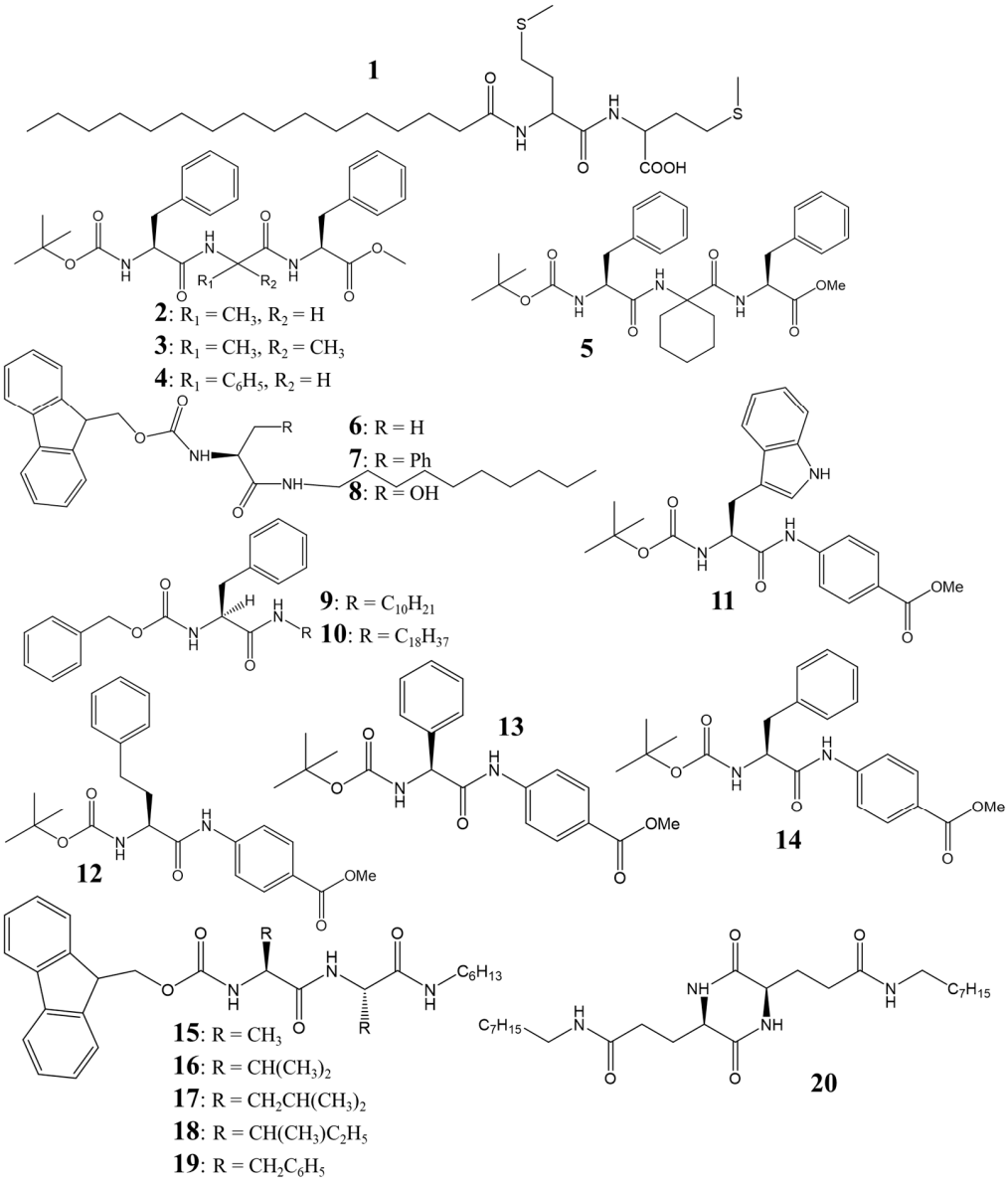


Figure 2. Chemical structures of PSOGs **1**–**20**.

More recently, two PSOGs **9**–**10** (Figure 2) based on L-phenylalanine derivatives were prepared by Abdellatif's research team [22]. These are easily synthesized, environmentally friendly, and biodegradable. Their phase-selective gelling ability was demonstrated with olive oil, sunflower oil, paraffin oil, and so on in the presence of water. The findings are very promising and may address many issues regarding oil spills and leakages in the river Nile and oil waste from industries. Chetia et al. [47] synthesized four dipeptide-based PSOGs with aromatic moieties **11**–**14** for oil spill recovery and dye absorption, while the organic solvent and the heating-cooling process were involved in the deployment of these organogelators. Similarly, Zhou et al. [48] also reported five dipeptide-based PSOGs **15**–**19** (Figure 2) for the removal of oil and toxic dyes, which can be applied in the powder form to

the biphasic mixtures of solvents and water at room temperature. Colak [49] demonstrated the glutamic acid-based PSOG **20** for fuel pollution control, which can be synthesized by a one-step reaction with up to 90% yield. The PSOG can congeal diesel, dodecane, and sunflower oil from the biphasic mixtures. Its biggest advantage is that it can be deployed without cosolvent and heating of the oiled water. The PSOG was dissolved in the water and heated to 80 °C to form an organogelator solution, and then the hot solution was applied to the water/diesel mixture for gelation at room temperature.

2.3. Carbohydrate-Based PSOGs

Carbohydrate and its derivatives are common building blocks in PSOGs due to their advantages of being widely available, easy to modify, and eco-friendly behaviour [17,50,51]. Generally speaking, most carbohydrate-based PSOGs are derived from glucose, galactose, and glucosamine, while some are synthesized by mannose and xylose [52]. With the advancement of synthetic methods and techniques, functional groups such as aromatic groups and long-chain alkanes are frequently introduced to sugar structures to enhance their solubility in organic solvents and improve their phase-selective gelling ability [37].

Vibhute and co-workers [17] reported five glucose-based PSOGs **21**–**25** (Figure 3) for marine oil spill recovery, and these sugar derivatives did not require the carrier solvents for deployment as they can be applied in the form of powder with good dispersion in the oil phase. Khayat and Zali-Boeini [53] further demonstrated in Figure 3 that the glucose-derived PSOGs **26**–**28** with multi-stimuli responsive properties were able to congeal various organic phases in the presence of water, and the organogelator **28** was used to remove the Sirri Island crude oil from seawater in the forms of dry powder and semi-dried gel with toluene at room temperature. The D-gluconic acetal-based PSOGs **29**–**31** with different lengths of alkyl chains were also synthesized and their gelation abilities were evaluated with hydrocarbon solvents [54]. Characterization analysis indicated that the gelation properties of PSOGs was the result of hydrogen bonding, π–π stacking, and van der Waals forces. Meanwhile, PSOG **29** was used to test its phase-selective gelation ability as a dry powder for a wide range of oils with viscosities varying from 0.4 to 8384.7 mPs. The results demonstrated that the gelling time and biphasic critical gelator concentrations were closely related to the viscosities of oils. Narayana et al. [55] demonstrated triazole-linked, N-acetylglucosamine based PSOGs **32** for both oil spill recovery and dye removal. Ethyl acetate was used as the carrier solvent for the PSOGs to take the phase-selective gelation tests with different API crude oils, and the results showed that the critical gelator concentration of gels was dependent on oil composition.

As shown in Figure 3, Pathak and co-workers [56] developed the second generation triazolylarabinoside-based PSOGs **33**–**34** for potential oil spill remediation, which can gel petrol, diesel, and crude oil in the biphasic systems, They investigated the structure and mechanical properties of gel samples using a series of characterization methods. They also found that the formed gel was both thermally and mechanically reversible through rheological experiments. Fan and co-workers [57] prepared several sorbitol-derived PSOGs **35**–**38** with hydrophobic alkyl or cycloaryl motifs through the modification of structural features. They found the phase-selective gelation ability was affected by the length of alkyl chain in PSOGs, with the longest alkyl chain yielding the best gelling ability. Similarly, another kind of sorbitol-based PSOG **39** was prepared through the reaction of sorbitol and benzaldehyde with a yield of up to 90% [58]. Rapid gelation with a wide range of oils is the biggest advantage of this PSOGs. For example, it can completely gel crude oil in less than 10 min at room temperature. However, Pathak and Yadav [21] achieved ultrafast gelation with crude oil (within 30 s) by using a blend of PSOG **40** (Figure 3) and starch at a very low loading and without any agitation. The mixing ratio of PSOG–starch in a 1:1 ratio proved to be most effective in gelling crude oil, as the starch played the role of solid support that enabled more homogeneous distribution of PSOG in the oil phase. Moreover, there is also a possibility that synergistic effects existed in starch as the adsorbent. Interestingly, the

authors also found that pure starch cannot congeal any solvents, including petrol, diesel, crude oil, and benzene.

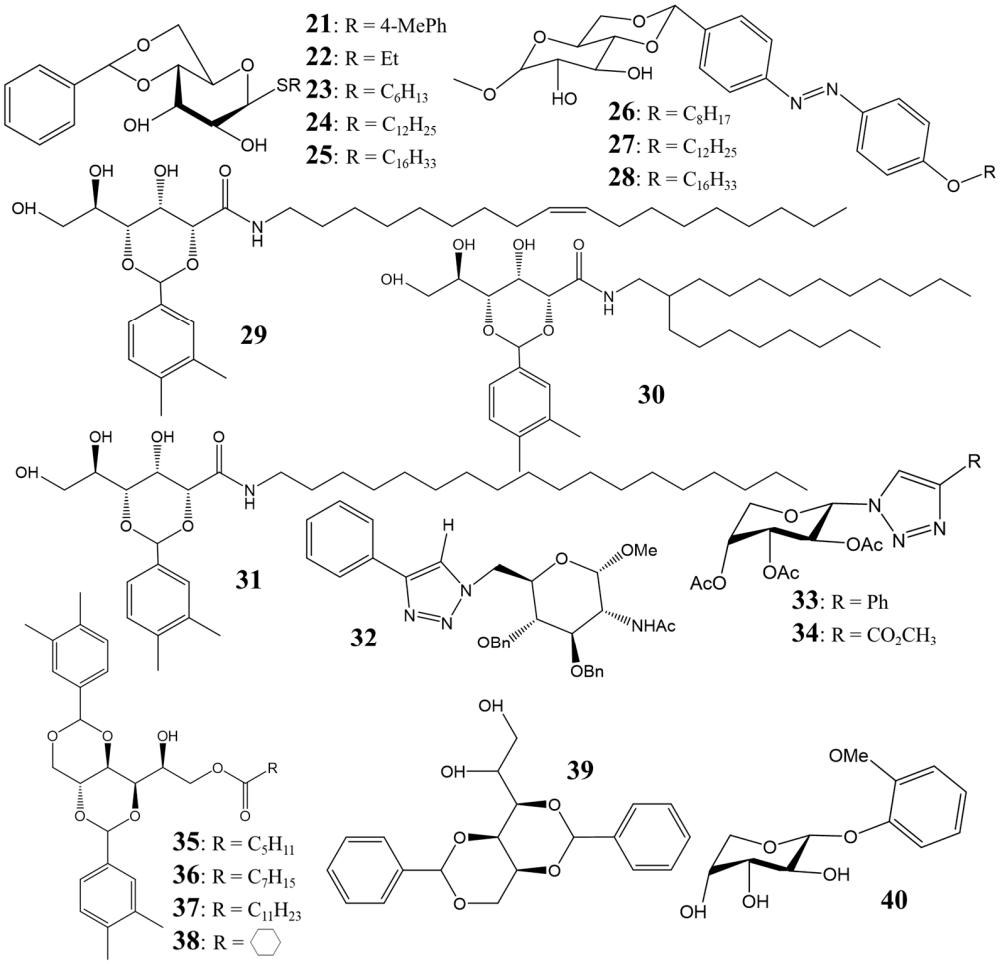


Figure 3. Chemical structures of PSOGs **21**–**40**.

2.4. Amide Derivatives

The small molecule organogelator derived from amides is regarded to be a very unique type of PSOG [44,59]. Datta et al. [25] demonstrated that the naphthalene diimide-based PSOG **41** (Figure 4) was able to achieve near instantaneous gelation with oils in the dry powder form. In their study, the powder of the organogelator (2.5 wt%) was applied on 25 mL of ONGC Mehsana heavy crude layer on a 150 mL saline water phase. It was observed that the oil phase completely congealed within 20 s without agitation or co-solvents. Surprisingly, it can also be used for the gelation of oil from biphasic systems at temperatures below freezing, which has rarely been reported before. An oleylamide-based PSOG **42** was reported by Eftekhari-Sis and co-workers [60], which can also gel a series of organic solvents in the form of xerogel under different conditions. Liu et al. [61] synthesized the pH-responsive PSOG **43** (Figure 4) by introducing the tertiary amine group, which can switch reversibly between hydrophobicity and hydrophilicity with pH adjustments. However, the heating/cooling procedure was involved in the dissolution of the PSOG in the oil/water system during the phase-selective gelation. This does not seem to be well suited for real oil spill incidents, because it is impractical to heat spilled oil and seawater during spill response.

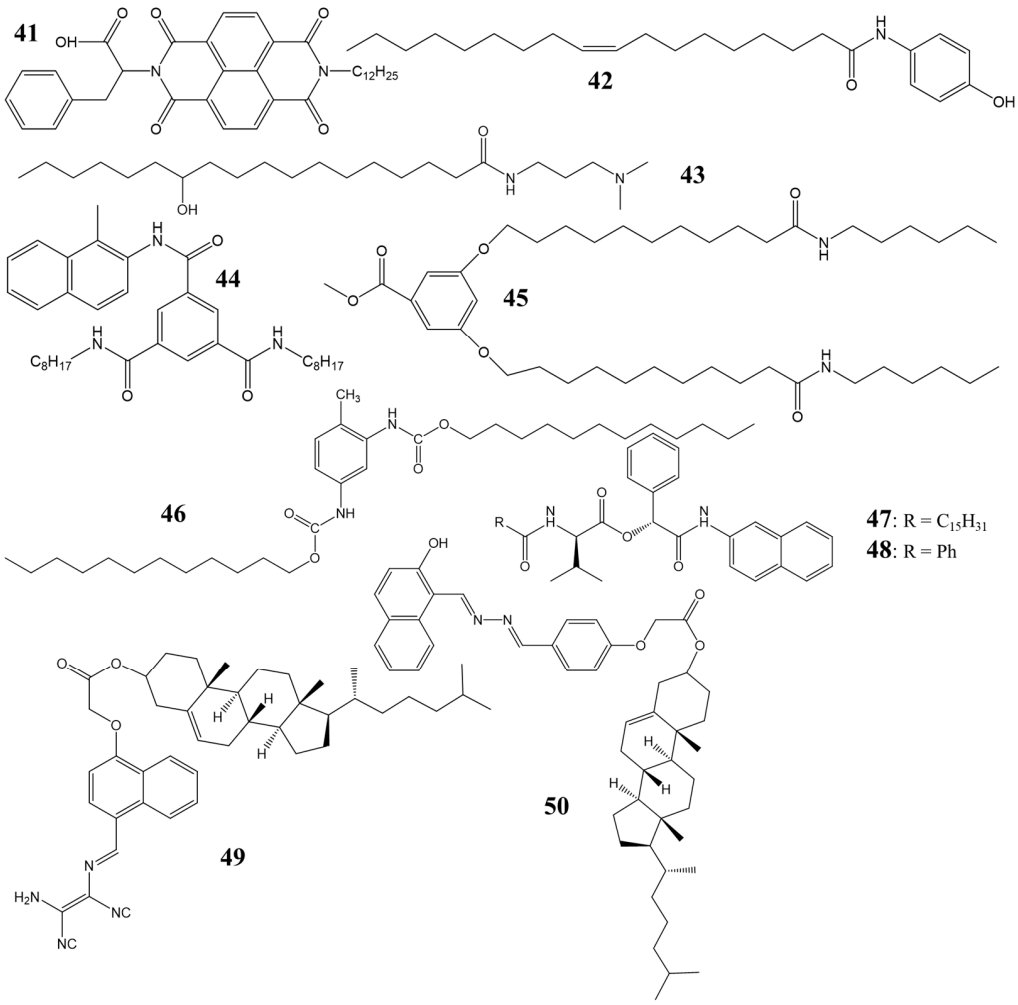


Figure 4. Chemical structures of PSOGs **41**–**50**.

According to Li and co-workers [62], the benzene 1,3,5-tricarboxamide based PSOG **44** can be used for not only aromatic solvents and oil recovery but also dye removal. The FTIR and UV analyses indicated that hydrogen bonding and π–π interaction accounted for the gelation process. Moreover, Zapién-Castillo et al. [63] observed the hydroxybenzoic acid bisamide-derived PSOG **45** (Figure 4) through characterization methods and evaluated its gelation abilities with organic solvents, diesel, and gasolines in both monophasic and biphasic systems. The phase-selective gelation of the organogelator was attributed to the intermolecular hydrogen bond of the amide groups, dipole-dipole interactions by esters, and the π–π stacking interactions by aromatic fragments. More recently, Bhardwaj and Ballabh in [19] demonstrated a design strategy for PSOGs on the basis of the aromatic/aliphatic-amide linker-bulky group, and they found that six synthesized compounds out of 13 demonstrated excellent gelation performance. Meanwhile, structure–property correlation analysis was also conducted to explore the gelation/non-gelation behaviour of PSOGs, which are affected by the aliphatic backbone, amide functionalities number, as well as the structure of the molecule terminal groups.

2.5. Organic Salts and Cholesteryl Derivatives

Previously, PSOGs based on organic salts were widely studied in the gelation of organic solvents and oils [64–66]. In recent years, there has still been some research on organic salt-based PSOGs for oil spill remediation. As shown in Figure 4, Wang and co-workers [67] reported the toluene diisocyanate-based PSOGs **46** that can selectively congeal oils from the biphasic systems to form thermal, reversible gels. The authors also explored

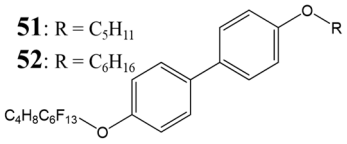
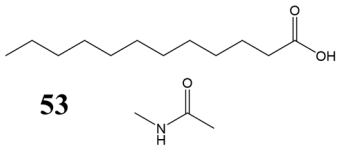
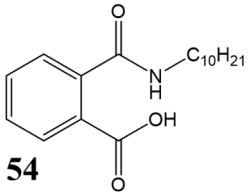
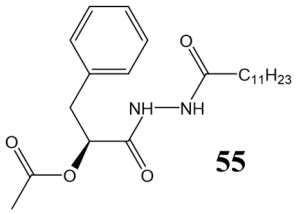
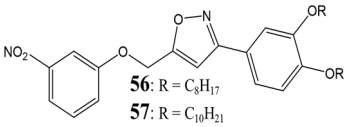
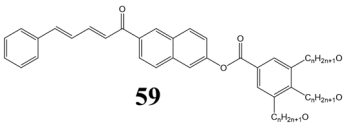
the deployment methods of the organogelator for real cases of oil spills in the forms of dry powder, co-solvents, and co-congealed solvents, and they finally chose gasoline as the co-congealed solvent to dissolve the PSOG for phase-selective gelation of oils from the water phase. Afterwards, a series of alkyl bicarbamate-based PSOGs containing various structures and lengths of alkyl chains were developed, characterized, and analysed for oil recovery in the presence of the aqueous phase by the same research team [68]. It was found that the self-assembled 3D network was driven by H bonding, π–π stacking, and van der Waals interactions, and the gelling ability was closely related to the structure and length of the alkyl chains, with medium length generating the most effective gelling performance. Zhang et al. [69] synthesized two PSOGs **47**–**48** (Figure 4) based on the scaffold of L-mandelic acid, and they then examined their gelation behaviours with organic solvents and product/crude oils in biphasic systems through the heating/cooling process. PSOG **48** showed better gelation performance compared with the other one. This might be attributed to an additional phenyl group for the enhancement of π–π interactions. In addition to the dry powder application form, this organogelator can also be attached to the filter papers to achieve effective oil removal in the presence of water.

Cholesterol derivatives are another wide-studied and versatile category of PSOGs, as they have the advantage of synergies between components, simple synthesis and modification of compounds, and excellent tunability [70–73]. However, few studies have adopted this kind of PSOG in the oil spill remediation. Raza and co-workers [74] designed and synthesized diaminomaleonitrile-functionalized PSOG **49** by linking diaminomaleonitrile as the H-bonding site to the cholesterol unit. It was considered to be the superior organogelator because it can successfully congeal 15 out of 20 solvents in the gelation tests. Similarly, the same research group developed the cholesterol-coupled diazine-phenol PSOG **50** (Figure 4) with multifunctionalities of phase-selective gelation, dye removal, and cyanide sensing [26]. For effective gelation, the naphthalene units provided the π–π stacking interactions, and the cholesterol moiety exerted the hydrophobic interactions to enhance the formation of the gels. In this phase-selective gelation experiment, the hot solution with the PSOG and the organic solvent was added to the oil/water mixtures, and it was found that the gel formed when the mixture cooled down and the aqueous phase remained unaffected.

2.6. Other Types of PSOGs

As indicated in Table 1, Cao et al. [75] demonstrated a novel class of PSOGs **51**–**52** based on 4-perfluoroalkylbutoxybenzene derivatives with liquid crystalline properties and phase-selective gelation behaviours. The driving force of the gelation was not hydrogen bonding but π–π stacking and weaker intermolecular interaction. However, this PSOG needs to be dissolved in a warm toluene solvent to be able to treat the oil/water mixture and achieve gelation at room temperature. A new deep eutectic solvent consisting of lauric acid and *N*-methylacetamide, without any synthesis procedure, was reported to be used as the PSOG **53** (Table 1) in oil spill recovery [23]. The two compounds are readily available, low toxic, and biodegradable, and they showed excellent phase-selective gelation properties after mixing into the deep eutectic solvent. Su et al. [76] developed a series of two-component PSOGs through the acid-base interactions from phthalic acid derivatives and n-alkylamine. The synthesized PSOG **54** did not require any purification procedures and can be directly used for the gelation of oil in biphasic systems, while it needed carrier solvents such as petroleum ether (5% ethanol) during the gelation process.

Table 1. Other types of PSOGs **51**–**59** with their structures and characteristics.

Structures of PSOGs	Description	Characteristics	References
 **51**: R = C_5H_{11} **52**: R = C_6H_{16}	Based on 4-perfluoroalkylbutoxybenzene derivatives	π–π stacking, the weaker intermolecular interaction	[75]
 **53**	A new deep eutectic solvent composed of lauric acid and *N*-methylacetamide	Do not require any synthetic procedure besides mixing	[23]
 **54**	The novel phase-selective two-component gelator based on phthalic acid derivatives and a linear aliphatic amine	One-step procedure alone without any purification, can be amplified to the kilogram scale	[76]
 **55**	Derived from phenyllactic acid with a hydrazine moiety, gelation of 17 kinds of organic liquids	Effective phenol removal and oil spill recovery with a satisfactory recyclability	[77]
 **56**: R = C_8H_{17} **57**: R = $C_{10}H_{21}$ **58**: R = $C_{16}H_{33}$	Based on an isoxazole backbone	Gel strength, and 3D structure related to length of the hydrocarbon chains	[24]
 **59**	A series of chalcone derivatives	Recover spilled oil, even in the presence of salts, acids and bases.	[78]

Sun et al. [77] reported the multi-functional PSOG **55** (Table 1) based on phenyllactic acid derivatives, the hydrazine moiety of which can effectively gel 17 types of organic liquids. This organogelator has the advantages of low cost, simple synthesis, as well as cheap raw materials, which further facilitate its application in oil spill remediation. Singh et al. [24] prepared a series of isoxazole-based PSOGs **56**–**58** through varying hydrocarbon chain lengths to address the problems of bisphenol pollution in water and oil spills. Additionally, the rheology, morphology, and driving forces of formed gels were well studied. Recently, a new class of PSOGs **59** (Table 1), derived from chalcone, were reported and showed great potential in oil spill recovery [78]. Their gelation ability can be attributed to interactions of π–π stacking, van der Waals, and hydrogen bonding, while the phase-selective gelation tests of the organogelator involved heating/cooling processes that are required to be tackled for future use in real cases.

Alkaline lignin/hemicelluloses were used for the preparation of the bio-based PSOG **60**, which can rapidly solidify 50 mL of crude oil from 1 L of seawater within the glass bathtub. This results from the synergistic actions between physical adsorption and chemical

condensates of PSOGs [79]. As shown in Figure 5, Shen and co-workers [80] illustrated that a novel bio-based PSOG **61** using the CNF and SiO_2 nanoparticles as raw materials was synthesized to gel a wide range of oils due to hydrophobicity interaction, network structures, and capillary action. It took around 10 min to completely solidify the crude oil using a dry powder form in the simulated spill scenarios, and the gelation time is expected to be shorter under agitation conditions. It provides a new direction for the development of PSOGs in oil spill remediation.

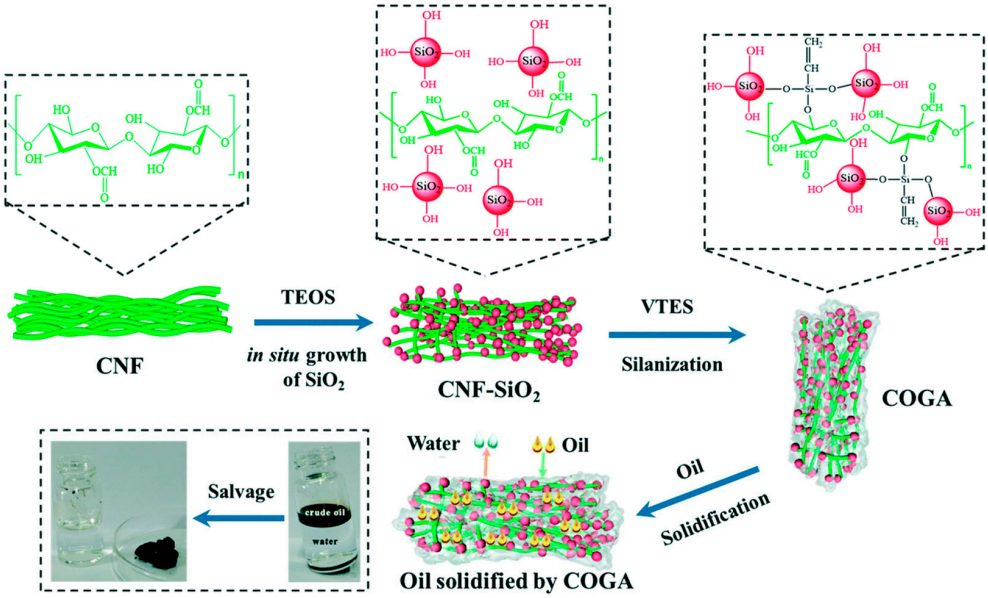


Figure 5. Schematic diagram of the PSOGs **61** preparation and the gelation mechanism for crude oil [80]: A 3D network structure was firstly constructed by the cellulose nanofibril (CNF), and then SiO_2 nanoparticles prepared in the mixture of tetraethyl orthosilicate (TEOS), ammonia, and ethanol were introduced on CNF by in situ growth to form CNF-SiO_2. Vinyl triethoxy silane (VTES) was used for hydrophobic modification of CNF-SiO_2 through a silanization reaction to form CNF-based oil gelling agent (COGA); The COGA was used to solidify the oil layer and the solidified oil was removed from the oil/water mixture.

3. Mechanisms of PSOGs

Various mechanisms are involved in the environmental and pollution control processes [81–84]. Typically, gels can be classified into chemical and physical gels [85,86]. The former often refers to polymeric gels that generate a 3D fibrous network through the covalent bond. The PSOGs belong to the category of physical gels, and their driving forces are noncovalent intermolecular interactions including hydrogen bonding, π–π stacking interactions, van der Waals forces, hydrophobic interactions, etc. [30,87]. Therefore, one major advantage of PSOGs is the thermos-reversibility especially during heating/cooling processes, which facilitates the recoverability of the organogelators and oils.

Among all noncovalent intermolecular interactions, hydrogen bonding is the most common driving force in the self-assembly process of gel formation, and it plays a crucial role in the gelation performance of the PSOGs [88–90]. For example, Singh and co-workers [24] uncovered that the proton of the isoxazole ring is vital to the hydrogen bonding interaction through temperature-dependent ^{1}H spectroscopy analysis, and then they further proved that hydrogen bonding is essential to the gelation behaviours in organic solvents via FTIR measurement. Similarly, both intermolecular and intramolecular hydrogen bonding interactions were responsible for the gelation process from the PSOG based on C-6 triazole-linked N-acetylglucosamine derivatives [55]. The authors found that the electron-withdrawing group of triazole rings enabled its proton to participate in the intermolecular hydrogen bonding interaction, while the intramolecular hydrogen bonding

was from the NH and OCH_3 groups. In addition, the $\pi-\pi$ stacking interactions existing in the phenyl ring of the PSOG also enhanced gel formation. Nandi et al. [41] confirmed that hydrogen bonding was the major driving force to the self-assembly process of the PSOGs by FTIR results, even though hydrophobic interactions of alkyl chains and $\pi-\pi$ stacking from phenyl groups were also helpful to gel formation. It is worth mentioning that in most of the reported PSOGs, the hydrogen bonding always acts as one of driving forces in the gel self-assembly process [25,44,45,68,78,91].

The $\pi-\pi$ stacking interaction is another common force that frequently occurs in the gelation process of PSOGs derived from aromatic groups [32]. It was reported that the PSOGs containing benzene rings showed better gelation performance than their counterparts with alkyl chains. This is because the $\pi-\pi$ stacking interaction presented by benzene rings participated in additional non-covalent interactions [17,62]. Soundarajan and Das [50] investigated the gelation mechanism of sugar-benzohydrazide-based PSOGs, and the UV–Vis analysis revealed that the interactions of $\pi-\pi$ stacking exerted by aromatic moieties in the PSOG are the main driving force for phase-selective gelation behaviours. Besides, FTIR results indicated that hydrogen bonding by -NH protons and the van der Waals force by long alkyl chains are involved in the gelation process to form 3D fibrous networks. For the toluene diisocyanate derived PSOGs, the $\pi-\pi$ stacking interactions exerted by the benzene rings, van der Waals interactions provided from alkyl chains, and double hydrogen-bonding related to the bicarbamate groups worked together to promote the aggregation and assembly process of PSOGs in organic solvents and crude oils [67]. For the sorbitol-derived PSOGs, π–π stacking was confirmed via FTIR studies for the formation of 3D fibrillar networks to entrap oils [58].

The van der Waals interaction is also one of typical supramolecular interactions, which is always exerted by long alkyl chains of PSOG molecules [92,93]. According to the work of Liao et al. [94], the gel formation of designed PSOGs was primarily due to the van der Waals interaction and intermolecular acid-base interaction. The van der Waals interaction frequently works with hydrogen bonding and/or π–π stacking interaction in the PSOGs as critical driving forces to achieve stronger self-assembly, leading to stronger gels [20,53,77,91]. Besides, the hydrophobic interaction, halogen bonding, and ionic interaction are also beneficial for the gel formation of PSOGs [62,74].

4. PSOG Deployment Methods

4.1. Application of PSOGs in Carrier Solvent

The use of carrier solvents refers to the dissolution of PSOGs in solvents, followed by the addition of the mixture into oily water to achieve phase-selective gelation of oil phase. It can be seen as a potential feasible deployment method in oil spill response with the advantages of uniformly distributing the PSOG molecules in organic phases and thus significantly accelerating the gelation speed [95]. However, it may be toxic to the marine environment and bring challenges for handling large amounts of solvents [88,96]. Tetrahydrofuran (THF) [20,24,26,41,57], petroleum ether [76], isopropanol [28], ethyl acetate [38,40,55], ethanol [46], oils including gasoline, diesel, crude oil [19,62,67], and toluene [45,75] are frequently used as carrier solvents to accelerate the gelation formation rate of the PSOGs.

In earlier times, Cao and co-workers [75] dissolved the 10 wt% of PSOG derived from 4-perfluoroalkylbutoxybenzene in a warm toluene solution for effective phase-selective gelation of synthetic lubricant from biphasic systems (oil/aqueous = 4:1, v/v). The 3D networks of oil/organogelator mixture rapidly formed in 1 min. However, if the carrier solvent was at room temperature, the gelation rate dramatically slowed down. Furthermore, it is reported that 0.5 mL of hot solution of the PSOG prepared with meta-xylene congealed 2 mL of crude oil from 4 mL of saline within a few minutes [56]. However, the PSOGs in the solvent mixture of ethyl acetate and ethanol can immediately solidify a wide range of oils with gentle (within 28–97 s) and vigorous (within 6–28 s) shaking at room temperature [43,44]. According to the study by Basu et al. [38], the PSOG from dipeptide derivatives in the carrier solvent of ethyl acetate (10% w/v) was the first to achieve phase-

selective gelation in less than 20 s using a 4 mL of 1:1 oil/saline water biphasic system. Narayana et al. [55] also dissolved 14 mg of synthesized PSOG into 0.2 mL of ethyl acetate to treat the oil/water (1:2) mixture and found that oil can be fully gelled within 15 min at room temperature.

THF is currently the most widely used carrier solvent for the dissolution of PSOGs. Fan and co-workers [57] prepared a series of PSOGs in THF for phase-selective gelation and concluded that the critical gelation concentrations were negatively correlated with the lengths of the alkyl chain of the PSOGs. As shown in Figure 6, the PSOG with the best performance dissolved in THF was shown to congeal 25 mL of gasoline from 225 mL of biphasic system in less than 3 min, and then the formed gel containing gasoline and PSOG was removed and recovered through a simple distillation procedure. Modal and co-workers [20] attempted three ways to disperse the PSOGs in the organic phase: heating/cooling, sonication, and use of the carrier solvent of THF, and they finally chose the method of creating a solution of the organogelator in THF to gel the diesel in the presence of water within one min. Similarly, the THF was also used to dissolve the PSOG for uniform dispersal in the oil phases, and the diesel phase was converted to gel in less than 60 s [24]. In some cases, the oil itself acted as the carrier solvent to separate the oil/water mixture. In the study of Bhardwaj and Ballabh [19], a series of PSOGs was developed, all of which can congeal diesel effectively. Therefore, the diesel solution containing 6–8% PSOG was chosen as the co-congealed solvent to solidify all the diesel in the biphasic phases.

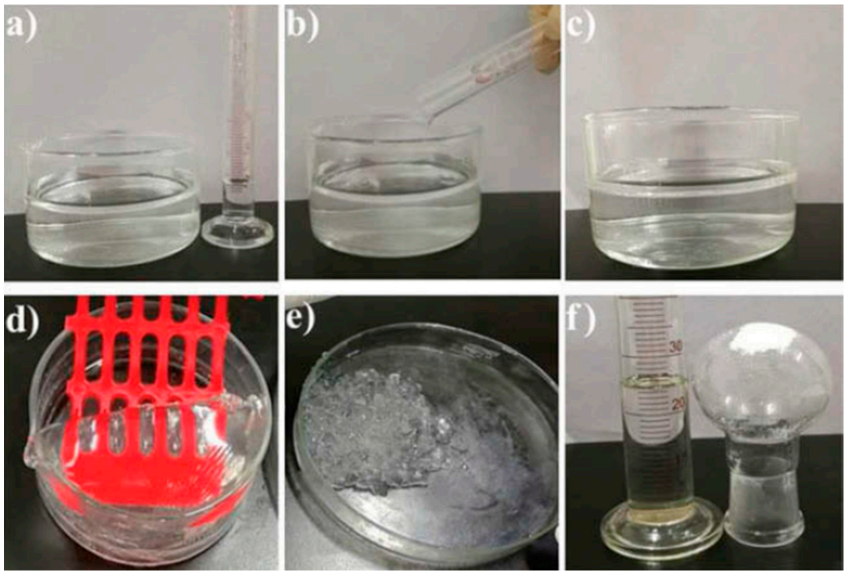


Figure 6. Removal of gasoline from oil/water mixtures using PSOG with a carrier solvent: (**a**) Biphasic system of gasoline and water; (**b**) PSOG in THF solution added to the gasoline layer; (**c**) Congealing the gasoline phase; (**d**) Removing the gel using a mesh device; (**e**) Removed gel; (**f**) Recovered gasoline and PSOG through distillation process [57].

4.2. Application of PSOGs in Powder Form

The application of PSOGs in powder form can avoid the involvement of water-miscible or -immiscible carrier solvents, thus alleviating detrimental effects to the marine environment and reducing the requirement for relative logistical and technical procedures [89,97]. The sugar-based PSOG prepared by Vibhute et al. [17] was directly sprayed on the crude oil layer from the biphasic system (oil/water = 1:10 by volume) in fine powder form at 1% of oil weight, and gentle stirring was conducted to make sure the PSOG was fully dispersed in the oil phase. However, the gel formation took a quite long time. Similarly, the glucose-based PSOGs in dry powder fully congealed crude oil with API 37 for 12 h, while its semi-dried form reduced the gelation time significantly, but it still took 90 min for complete gelation [53]. To address the problem of the low gelling speed, Ren and

co-workers [95] developed a previously unexplored method through acetonitrile-wetted PSOG powders to dramatically accelerate the gelling rate of various oils. Under optimal wetting conditions, the gelling speed of heavy oils can reach over 100 times more than that of dry powder. Qu and co-workers [98] also tried the wetting powder strategy with the use of ethyl acetate for their PSOGs, derived from the p-alkoxybenzoyl group, but the results of 3-h gelation did not work out so well, so they finally decided to use the carrier solvent of toluene (0.5 mL) containing 0.1 g of the POSG to achieve rapid gelation for 0.8 g of crude oil in the presence of water (100 mL) within 30 s.

As shown in Figure 7, Zhuan et al. [58] developed the sorbitol-based PSOG and applied 0.01 g of its powder form in the mixture of 1 mL of various oils and 4 mL of water with suitable stirring. The gels formed only after several minutes. Similar deployment processes also can be found in the studies of [54,69]. The PSOG derived from phenyllactic acid can congeal various petroleum products within several minutes in the dry powder form, and it did not require any heating, carrier solvents, or stirring procedures [77]. The naphthalene diimide-derived PSOGs reported by Datta et al. [25] achieved near instantaneous gelation. In detail, the 2.5 wt% dry powder of the PSOG was sprayed on the entire heavy crude oil layer (25 mL) in the presence of saline water (150 mL), and it only required less than 20 s for complete gelation without any agitation or wetting. This indicated that this PSOG is a very practical and promising candidate for oil spill clean-up.

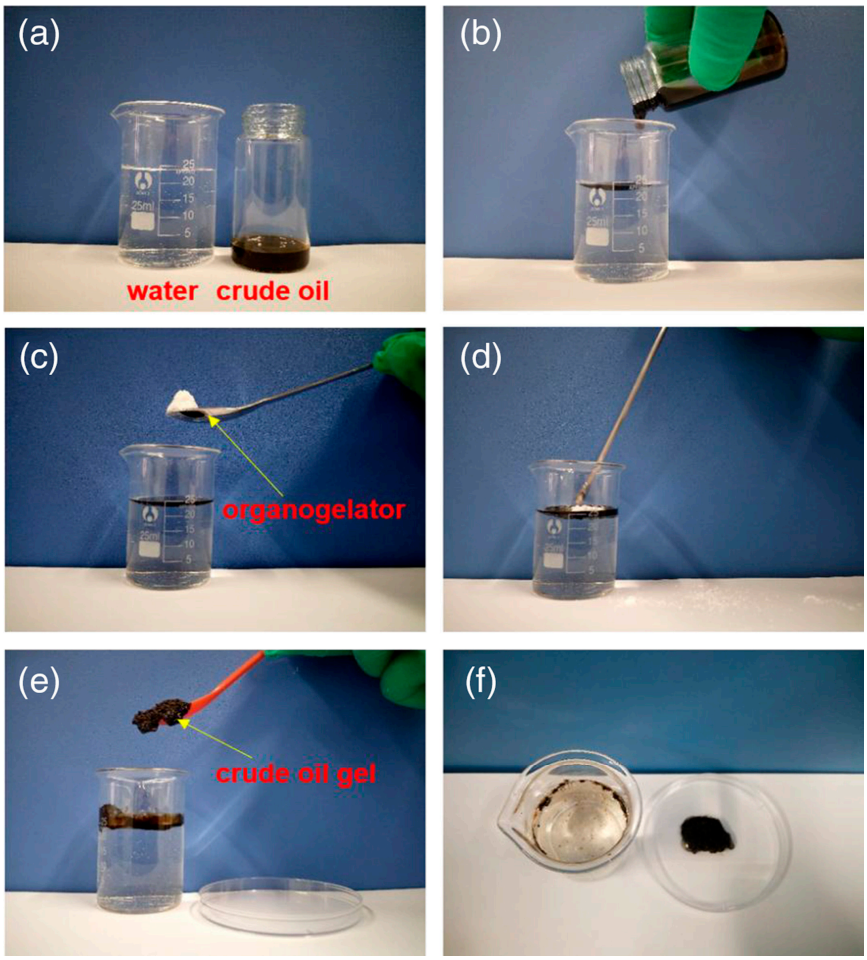


Figure 7. Removal of crude oil from oil/water mixtures using PSOG in the form of dry powder: (**a**) Single-phase water and crude oil; (**b**) Adding crude oil to the water phase; (**c**) Putting the PSOG powder on the crude oil layer; (**d**) Dispersing the PSOG powder into crude oil by stirring; (**e**) Removing the solidified oil using a spoon; (**f**) The water phase after removing crude oil and the formed gel [58].

4.3. Other Potential Application Methods

The environmental processes can often be affected by different factors [99–102]. The response requirement and site conditions also need to be considered in the selection of application alternatives. Apart from the above two deployment methods, there are other practical techniques that have great potential in real oil spill remediation. The PSOGs were frequently attached on suitable substrates to act as sorbents to remove the spilled oil. Prathap and Sureshan [103] incorporated the sugar-based PSOG into the cellulose pulp, making the cellulose fibres hydrophobic. The oil from the biphasic system can be absorbed on the hydrophobic fibre, and then the attached PSOG uniformly dispersed in the oil phase and self-assembled by hydrogen bonding to the cellulose, solidifying the oil. Furthermore, Zhang et al. [69] synthesized mandelic acid-based PSOGs that can be directly used in powder form with 30 mg of PSOG, congealing up to 0.1 mL of crude oil in the presence of seawater, while the organogelator coated filter papers were prepared by the attachment of the PSOG. Their efficiency of oil removal can be up to around 80%. Compared with the deployment of dry powder, coated filter papers dramatically decreased the doses of PSOG, alleviating the burden on the affected environment. Similarly, the vanillin-derived PSOGs reported by Das and co-workers [91] were evenly coated on the highly porous polyurethane sponge, making it more hydrophobic with the water contact angle over 138°. The PSOG-coated sponge demonstrated a significant increase in oil absorption ability, around 55 times of its original weight. The PSOG-assisted technique was also successfully demonstrated on other substrates, such as fibrous cotton.

As mentioned above, Pathak and Yadav [21] developed a novel solid deployment method using the PSOG/starch blend to congeal the crude oil, and the results showed the 24 mg of blend in the ratio of 1:1 for PSOG and starch had the best phase-selective gelation performance. It gelled 3.5 mL of oil within 30 s without any stirring and heating procedures. Nevertheless, Eftekhari-Sis et al. [60] demonstrated the oleylamide-derived PSOGs and deployed them in the form of a xerogel by evaporating the solvent to congeal oil. In the test of phase-selective gelation, 0.5 mL of hexane was adsorbed in less than 3.5 min in the presence of water with the use of 0.1 g of PSOG xerogel. It is worth mentioning that a novel nanomagnetic PSOG was designed by Yousofi and Rahmati [104], and then it was investigated for its gelation ability with petroleum derivatives (gas, diesel, and kerosene) from a water phase. However, the deployment of the PSOG involved sonication and heating/cooling procedures that may prevent its application in large-scale oil spill incidents.

5. Conclusions and Recommendations for Future Research

Research on PSOGs has made significant progress in marine oil spill remediation, especially over the last seven years. In this review, the potential of PSOGs as promising candidates was systematically explored from the perspectives of molecule structures, mechanisms, and deployment methods. Extensive laboratory tests have demonstrated that PSOGs have the advantages of biocompatibility, efficiency and safe operation, great oil removal ability, and high resource recovery rate. This has a great significance for the technological progress of oil spill treatment. However, there are still challenges for the practical, large-scale application of PSOGs at sea due to the lack of standardized testing protocols, difficulties in field tests, and gelation selectivity.

It has been over 20 years since the first PSOG was reported. However, some challenges in the application of the PSOGs for oil spill recovery still remain. First, there is no standardized testing protocol to assess the phase-selective gelation performance of the PSOGs, which can be affected by various variables such as doses, deployment methods, oil types, reaction time, temperature, etc. It is difficult to compare the performance of PSOGs in different studies as most authors adopted their own methods to evaluate gelation effectiveness. In response to this challenge, developing a well-accepted and easy-to-implement testing protocol for the evaluation of the PSOGs' performance is essential. Second, a sound decision-making process may involve the consideration of different factors [105–107]. It is expected that a comprehensive evaluation framework to systematically assess the PSOGs

for oil spill recovery from aspects of effectiveness, toxicity, cost, scalability, stability and so on will be developed, which will be beneficial for decision making and future field applications [108]. Third, the PSOGs usually work very well with light crude oils, while their performance is dramatically inhibited when it comes to heavy crudes or asphalts and resins as the molecules cannot be evenly or rapidly dispersed in the oil phase, resulting in incomplete or slow gelation. This dilemma requires the development of a new generation of PSOGs without gelation selectivity or adaptation of the existing development method to efficiently diffuse the PSOGs within the oils.

The developed PSOGs were mainly tested in laboratories, especially in small vials or beakers with limited amounts of oil and water. Laboratory demonstrations cannot be representative of all field conditions such as wind, sea waves, mixing energy, sunlight, and affected scale, which can have effects on the effectiveness of the PSOGs. The containment and recovery of PSOGs with oils need to be well guaranteed if this technique is deployed in real cases. However, the lack of field testing and application prevents this technology from being well considered and promoted in the decision-making process [16]. The use of the meso-scale system to simulate the actual response environment would be a good choice when field tests are not available or permittable. For example, a meso-scale tank simulator considering the effects of tide and waves at sea could be constructed to investigate the performance of the PSOGs. The results would be more reliable and convincing.

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