Overview of methods in Oil spill technology

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Abstract. Over the decades oil spills have been the biggest threat to the aquatic life and to a nation’s economy. Many methods were suggested in the literature to remove the oil that is present on the surface of sea water after the spill. Hydrogel formation is one of the best technique that could be adopted to handle oil spills. Since the oil spill is a oil and water emulsion, formation of hydrogels with these emulsions could lead to the recovery of oil. The formation of hydrogels can be either physically crosslinking the polymer molecules or covalent bonding among the entangled polymer molecules. The methods of making the hydrogels conceivable to acquire surface hydrophobicity and oleophilicity. Hydrogel technology could be more cost effective and efficient in recovering the oil from the spill, eco-friendly and easy to use. It is proposed that the hydrogels could be potential candidates for handling the oil spills. The methods described in this review explains the various hydrogels that could be utilized for oil spill recovery.

1. Introduction
Oil spills are known to be destroyers of animal and marine life. The biggest oil spill was ever happend in the Gulf of Mexico in 2010 has been known to damage most marine and animal life. It was estimated that the spill went around 68000 square miles in the sea affecting the life of 1 million sea birds, 1000 sea turtles and 5000 marine animals. Extensive efforts were used to remove the oil spelt on sea water and these methods were proved to be expensive and non-efficient[1, 2, 3, 4]. It became essential to develop a new cost effective and efficient method to handle oil spills. Various methods were suggested that include sponges that preferentially dissolve oil[5], membranes and meshes[6], small buoyant devices[7]. Because of the limitations of capillary effects during the diffusion of oil into these porous structure, hydrogels could be best candidates of the oil spill recovery. Following are the important methods that would be useful in oil spill recovery techniques using hydrogels.

2. Hydrogels for oil spill recovery
Crude oils with high viscosities could not be separated out with simple methods. Robust poly ionized hydrogels coated on a membrane made of polyacrylate-grafted poly (vinylidene fluoride) were suggested to be efficient. The method of preparation of this kind of membrane is a simple one-step alkaline-induced phase-inversion process. These materials exhibit extraordinary anticrude-oil-adhesion property and strong hydration capability. These materials possesses ultralow oil adhesive superoleophobicity for viscous oils in the presence of water. These are proved to be self-cleaning. They have extensively high flux and oil rejection when overlaid on copper mesh. These polymer’s surfaces are little rough and then gets smoothened when immersed
in an aqueous solution. These materials have good water uptake properties. During the alkaline-induced phase-inversion process, PAA was converted to sodium polyacrylate (PAAS), which has a substantially higher hydration capability, resulting in better oleophobicity, anti-oil-adhesion property and extremely low oil adhesion. It is found that these hydrogels coated on a copper mesh showed excellent anti-crude oil fouling properties. The major advantage of these materials being the recycling and are driven by gravity with in a pH range of 5 to 12[8, 9].

Guar gum is a natural polymer consisting of alternating lateral branching of galactose groups and linearly bound mannose units. When guar gum hydrogels are coated on a stainless steel mesh and tested for oil spill recovery, these meshes showed extremely low underwater oil adhesive properties. Guar gum coated meshes proved to be used for several time after coating the mesh with a fresh coat of hydrogel. These materials systems showed selective and efficient separation of oil and water with high water fluxes using gravity alone. These systems shows excellent oil repellents, easy-cleaning , biocompatible and biodegradable attributes towards environment and the capacity to be used for a long time and cab be recycled. After 6 cycles, the separation capacity of the guar gum hydrogel-coated mesh remained similar[10].

chitosan-alginate (CS-ALG) hydrogel coated mesh with outstanding underwater superoleophobicity, anti-oil fouling performance and surface microstructures achieved by a simple two-step dip-coating process powered by gravity without any external energy usage. This provides super-wetting surface, wetting behaviours, high flux durability in hypersaline environments. The fast gelation process due to Alginate-based hydrogel coatings results in reducing mechanical properties. To overcome this it is coated on copper mesh to achieve the maximized electrostatic interaction. When submerged in water, the hydrogel-coated mesh demonstrates outstanding underwater super oleophobic properties. The combined impact of its rough micro/nanostructure and large hydrophilic groups on the hydrogel coating surface may be responsible for these unique wetting characteristics. Furthermore, oil droplets quickly flow off the surface of the hydrogel coating, showing its low oil adherence and anti-fouling properties[11].

Non-toxic blends such as poly(vinyl alcohol)(PVA) combined with starch or chitosan were proposed for the oil spill recovery. Combination of PVA and starch shows higher absorption capacity compared to the PVA chitosan combination. These mixtures were made in the presence of water/DMSO as a co-solvent and in a surfactant-free emulsion polymerization. These blends showed uniform structure and suggested for the suitable candidates for the oil spill recovery. These materials exhibited good mechanical, thermal and tensile strength. As roughness is advantageous for oil absorption, PVA starch combinations showed indicating more roughness. This method of removal of oil from the spill does not require oil burning to recover, rather simple roll squeeze is sufficient[12].

The radiation induced graft polymerization hydrogel based on chitosan and polyacrylamide is proposed as a suitable candidate for the oil spill recovery. The hydrogels were prepared based on the varying concentration of acrylamide and with different irradiation intensities. In these materials acrylamide gets successfully grafted onto chitosan backbone. These showed thermal properties which suggests occurrence of structural phase transition. It is also observed that with high radiation doses, the produced hydrogel’s crosslinking rises resulting in a significant reduction in swelling capacity which can’t hold large amount of water. The porosity of prepared hydrogels are obvious and rough and they are evenly distributed[13].

Cellulose on the other hand is the most prevalent natural polymer having significant advantages such as renewability, environmental friendliness and biodegradability. It’s an excellent option for oil spill clean-up because it has a large number of hydroxyls throughout the chains, which give cellulose its hydrophilicity. The use of a non-derivatizing aqueous solvent to convert cellulose is advantageous since it is cost-effective, inert and chemically stable. Separation performance may be influenced by the electrolytes found in oceans. To fabricate hydrogels cellulose is dissolved in water and lithium hydroxide is used as a cross-linker.
Because of abundance of hydroxyl groups in cellulose it form physically cross-linked cellulose hydrogels. Underwater oleophobic characteristics and high flux oil/water separation efficiency and recyclability are demonstrated using hydrogel coated mesh structures in oil spill recovery. The separation efficiency of the cellulose hydrogel coated stainless mesh remains unchanged after several recycling cycles[14].

Hydrogels based on chemically etched on a succession of copper foams with super-hydrophobicity and super-oleophilicity using $FeCl_3/HCl$ solution and constant ultrasonication were proposed for oil spill recovery. The polymeric fibres were electrospun by dissolving polystyrene in a solvent of chlorobenzene and a non-solvent of dimethyl sulfoxide. Oil was recovered using a small boat constructed of prepared copper foam, a string bag of as-spun PS fibres with high oil absorption capacity, or a porous boat inserted with electro spin fibres. The fabricated and modified Cu foams were utilised to separate oil from water using five distinct types of oil with various viscosities and three different organic solvents[15].

The resulting hydrogel-covered filtered paper with numerous crosslinked networks between cellulose filter paper is a proposed oil spill recovery material. Hydrophilic PVA with glutaraldehyde acting as a crosslinker in acidic condition forms hydrogels of varying cross-linking networks. These materials are proposed as powerful tools to isolate oil–water combinations in extremely acidic, basic, and salty environments. The method would result in the creation of numerous crosslinked ether bond/acetal ring bridging networks. The results indicated that the hydrogel covering may successfully lower the attraction for oil droplets in a variety of ways. Additionally, the super-hydrophilicity and underwater super-oleophobicity of hydrogel-coated filter paper, as well as ultra low oil adhesion, permeate flow, and densely interlaced structures, are important for the separation of oil-in-water emulsions. These filters can provide the same level of efficiency for up to 30 cycles[16].

To separate oil and water, a simple and quick (within 5 minutes) candle-soot approach to in situ manufacture super-hydrophobic coatings on porous copper foam materials is often utilised. However, because of its great porosity and mechanical robustness, copper foam is one of the finest and optimal methods for oil spill recovery separation. In this, a two-layer micro/nano structure was created and to modify the surface copper oxide was used. The produced copper foam demonstrated good robustness, super-hydrophobicity, and super-oleophilicity, as well as extremely effective oil/water separation and long-term recycling performance. It was also simple to operate, quick to respond, and inexpensive in cost[17]. Various hydrogel coatings and different polymeric and non-polymeric systems that were suggested for the oil spill recovery are as given in Table 1.

3. Hyaluronic acid hydrogels for oil spill recovery

Based on the data available in the literature, the hydrogel which are hydrophilic in nature and form strong gels are the potential candidates for the use in oil spill recovery systems. It is found that hyaluronic acid, a natural polymer, has potential use in oil spill. Hyaluronic acid, a mucopolysaccaride occurs essentially in all living organisms. It has biological functions such as maintenance of elasticity in joint tissues, maintain the jelly nature of vitreous fluid, control tissue hydration, water transport and many more[18]. Hyaluronic acid also known as hyaluronan consists of repeating units of N-acetylglucosamine and glucuronic acid. The structure of hyaluronica acid is as shown in Figure 1.

Hyaluronic acid (HA) is a long chain molecules whose molecular weight extends upto millions of Dalton[19]. In the present work, hyaluronic acid with a molecular weight of 1270 kDa was considered to make hydrogels by crosslinking with divinyl sulfone (DVS). 0.5 g of hyaluronic acid was dissolved in 0.075, 0.1, 0.125, 0.15 and 0.2 M solution of sodium hydroxide to make the solution alkaline. The idea behind making the alkaline solutions is to mimic the alkalinity of sea water. It is also evident that the crosslinking of hyaluronic acid with divinyl sulfone happens in
Table 1. Different hydrogel systems suggested in the literature for oil spill recovery

| S.No | Materials                                                                 | Method                      | Efficiency (%) | Reference |
|------|---------------------------------------------------------------------------|-----------------------------|----------------|-----------|
| 1    | Acrylamide and methylenebisacrylamide                                     | Polymerization              | 80-92          | [9]       |
| 2    | PAA-g-PVDF powder and dimethylformamide                                   | casting                     | upto 97.1      | [8]       |
| 3    | Guar gum and sodium metaborate                                            | cross-linking               | 97.45-99.70    | [10]      |
| 4    | Sodium alginate, chitosan and ginpin                                       | ionic cross-linking         | 97-99          | [11]      |
| 5    | Poly (vinyl alcohol), chitosan and starch                                  | casting                     | upto 96.3      | [12]      |
| 6    | Chitosan and acrylamide                                                  | irradiation                 | upto 99        | [13]      |
| 7    | Cellulose, urea and lithium bromide solution                              | casting                     | 98.89-99.43    | [14]      |
| 8    | Copper foam                                                               | Chemical etching            | 95-97          | [15]      |
| 9    | Poly(vinyl alcohol) and glutaraldehyde                                    | cross-linking PVA on filter paper | up to 99.9 | [16]      |
| 10   | Copper foam                                                               | Casting                     | 87.7-98.1      | [17]      |

Figure 1. Structure of hyaluronic acid

alkaline conditions. The solutions of HA thus prepared were carefully measured for its pH value and noted. These gels are analysed in the rheometer using a cone and plate geometry to obtain the gel strength using oscillatory shear rheology, as shown in Figure 2.

It is evident from Figure 2 that the gelation strength, which is storage modulus of the gel, varies non-monotonically with the the alkalinity of the solution. However, these changes were not in the orders of magnitude difference. Hence it can be concluded that these material systems under highly alkaline conditions upon crosslinking of hyaluronic acid with divinyl sulfone exhibit excellent gel strength. The conformational changes of the hyaluronic acid molecule leading to these differences since the alkalinity of the aqueous HA solutions make the HA molecule to break into smaller fragments. But it is to be noted that the cross-linking of HA molecules overcomes the degradation and forms strong gels. It is now understood that the cross-linked hyaluronic acid hydrogels are potential candidates to be used in the oil spill recovery systems. The another
Figure 2. (a) Variation of pH of the aqueous hyaluronic acid solutions made with different NaOH Molarities (b) Variation of gel modulus for various hydrogels of hyaluronic acid

advantage of these hydrogels is that hyaluronic is highly hydrophilic and could result in better oleophobicity when used in the oil spill recovery.

It is proposed that required concentration of hyaluronic acid solutions could be made by dissolving HA in alkaline solution. The metal mesh which is to be coated with hydrogel is dipped into these solutions and dried for sometime. These meshes are further dipped in the divinyl sulfone solution for required period of time to complete the cross-linking of HA molecules. This method is being simple and inexpensive and a simple dip-coating works out the formation of hydrogels, this material system could be proposed best suitable for oil spill recovery. The coated meshes are then utilized to test the oil recovery from the spills.

4. Conclusions and future perspectives
It is clearly evident that the hydrogels when coated on the metal meshes exhibit peculiar characteristics that could be used to separate oil from oil spills. Many of the hydrogels were proposed that form hydrogels with simple casting, physical and chemical cross-linkings, irradiations with different kinds of polymers. It was also shown that chemical foam with etching of metal on the surface of the mesh could also induce the separations. The motive of all these kinds of separation being cost effectiveness and efficient methods, hyaluronic acid hydrogel coating on the metal meshes could be potential candidates for the oil spill recovery. The initial characterization of these hydrogel showed that they could form potential hydrogels upon cross-linking and could withstand the alkaline conditions. These material systems could be tested for the efficiency of separation upon coating the hydrogels on the metal mesh.

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