

Review

Materials and Technologies for the Tertiary Treatment of Produced Water Contaminated by Oil Impurities through Nonfibrous Deep-Bed Media: A Review

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Abstract: This review covers various aspects of the treatment of emulsified oil/water mixtures and is particularly focused on tertiary treatment, which means the reduction of the oil content from 70–100 ppm to below 10 ppm, depending on national regulations for water discharge. Emulsified oil/water mixtures frequently occurs in water treatment processes because, in the petroleum industry, chemically enhanced oil recovery leads to the production of a vast amount of oil-emulsified wastewater. This review is focused on various aspects of tertiary treatment via granular deep-bed filtration. The importance of polymeric materials, as well as carbon nanostructures, which may be an alternative to the current media have been highlighting. The particular potential of polymers is based on their broad availability and low price (particularly for polyolefins), the simple treatment of their surfaces through a variety of chemical and physical methods to design surfaces with tailored surface free energy (wettability), and the porosity. Polymer technology offers a variety of well-established methods for designing foams with tailored porosity, which, together with appropriately tuned surface energy and controlled roughness, would open new avenues for the production of foamy media for efficient oil/water separation. Additionally, a crucial inventions in deep-bed filtration is discussed.

Keywords: produced water; tertiary treatment; deep-bed media; foams; filtration; adsorption; coalescence

1. Introduction

Oil and grease (O&G) are organic substances composed of hydrocarbons, fatty acids, soaps (surfactants), lipids and waxes. Petroleum wastewaters from various sources (crude oil, gas, shale gas extraction and oil refineries) represent the largest volumes of oily polluted waters, followed by metal processing wastewater and food processing wastewater [1].

As an illustration, the global volumes of produced water volumes were 202 billion barrels in 2014 and were estimated to be approximately 340 billion barrels in 2020 [2]. The estimated produced water volume from shale reservoirs over the first 5–10 years of production ranges from 1.7 to 14.3 million liters per well [3].

Wastewaters from the petroleum industry typically contain a high content of aromatic compounds such as benzene, toluene, xylene, and polyaromatics. These compounds have mostly nonpolar and aliphatic character and interact with other substances through weak dispersive (London) forces or

aromatic structures, which can additionally interact via so-called π - π stacking (interaction between adjacent aromatic rings) [1]. Emulsification of oil is another phenomenon occurring in water treatment processes because emulsifiers and surfactants alter the chemical character of an oil droplet surface. In the petroleum industry, chemically enhanced oil recovery (EOR) leads to the production of a vast amount of oil-emulsified wastewater because surfactants (together with polymers and alkaline compounds) are key additives that are flooded into wells in order to enhance the recovery of bypass oil and oil trapped in porous reservoirs [4]. Sandstone reservoirs are mostly treated by anionic surfactants, whereas carbon reservoirs are treated by cationic surfactants [5]. This difference is due to the different charges of the substrate on which oil is adsorbed; thus, surfactants with different charges are used to enhance the desorption of oil from the substrates, which may play a role in later water purification processes. More details about various aspects of EOR and applied surfactants can be found in the review of Gbadamosi et al. [6]. On the other hand, wastewaters from the agriculture and food industry are mostly polluted by natural oils and waxes, which are generally esters of fatty acids (carboxylic acids consisting of saturated and unsaturated hydrocarbon chains and terminal carboxyl group(s) and glycerol) [7]. These compounds are more polar than previous compounds and can interact with substrates through stronger van der Waals forces (dipole-dipole, dipole-induced-dipole, and hydrogen-bonding interactions) [1]. Regardless of the oil's chemical composition, the water/oil mixtures can also be classified according to the size and morphology of the oily phase (Table 1).

Table 1. Physical classification of O&G droplets (adapted) from Patterson [7] and Rhee et al. [8].

Physical State	Diameter Range	Description
Free oil	>150 μm	Droplets that rise quickly to the surface in quiescent conditions due to an imbalance of forces caused by the differential density between oil and water
Dispersed oil	20–150 μm	Droplets stabilized by electric charges and other interparticle forces
Emulsified oil	20 μm	Droplets stabilized by the chemical action of surface-active agents
Soluble or “dissolved” oil	<5 μm	Dissolved or very finely dispersed droplets
“Oil-wet solids”		Suspended solids with oil adhered to their surface

Treatment of oily polluted wastewaters depends on the oil content and can be categorized as primary, secondary and tertiary treatment. While primary wastewater treatment is mostly removing solid matter from wastewater via gravity driven processes, secondary treatment further purifies wastewater by various chemical or physical based treatments [1]. Tertiary treatments include purification of wastewater consisting of approximately 70–100 ppm of oil impurities, and the required outlet is below 5–10 ppm [1]. Figure 1 summarizes various methods for primary, secondary and tertiary treatment of oil/water separation. Treatment line can be tailored based on particular composition of produced water to meet requirement for water, which will be discharge at the end. Usual decrease of oil is from 10,000 ppm down to few ppms. Detailed elaboration of various treatment media are reported [8,9].

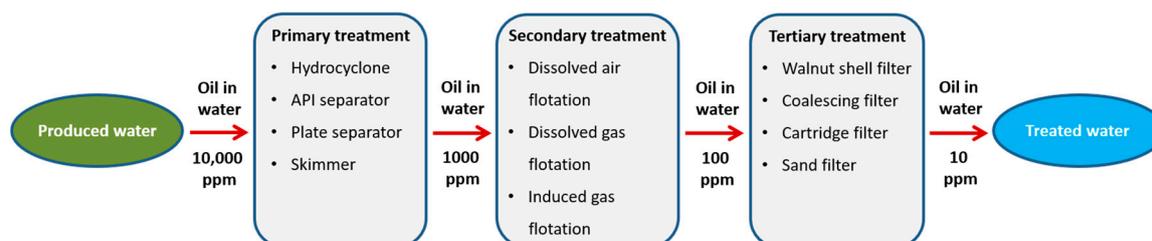


Figure 1. Schematic illustration of various treatments for oil/water separation.

This review is focused on various aspects of tertiary treatment via granular deep-bed filtration.

Other tertiary treatments include nanofiltration (NF), reverse osmosis (RO), biological treatment, oxidation (particularly based on Fenton's reactions), and sorption in batch systems [1]. Oil removal by sorption through batch systems and percolating column configurations have some common features (interaction of oily pollutants with adsorbent media, diffusion of oil into the adsorbent), but they differ in some aspects [1,10]. Fine powders, which are frequently used in batch systems (activated carbon, modified silica, clays, etc.) are not applicable in flow systems (deep-bed filtration) due to significant pressure drop when liquids pass through an adsorbent, resulting in a decrease in the flux of the penetrating liquid. Another drawback of fine powders is that oil droplets occupy the entrance of the pores and thus block a significant part of the contact surface area [11]. Accordingly, the adsorbents used for deep-bed filtration have mostly granular forms (in the case of natural products including walnut shell, cork, etc.) or uniform spherical shape (synthesized resins) with an appropriate size to compromise the need for a large surface area (enhanced adsorption) and a sufficient flow [12]. Advantages of an approach based on sorption are high removal efficiency, no reactant consumption, simple operation, low cost, no production of byproducts, and continual or discontinuous adsorbent regeneration resulting in long-term use [13]. A drawback is an insufficient removal efficiency for finely dispersed emulsions. Media that support efficient emulsion separation can induce significant oil droplet coalescence, as will be discussed later.

Sorbents of an appropriate size and shape can be prepared by grinding suitable natural products (walnut shell, chitosan-rich structures) or synthetic polymers or through a direct synthesis of polymeric materials with tailored geometry and surface properties. In particular, polymeric materials represent the most prospective sorbents for potential use in filtration setups due to their high stability, selectivity, low cost and variability of their internal and external morphology and mechanical, thermal and particularly surface properties controlled by the selection of suitable polymerizable monomers and by the type of synthesis [1]. The surface of those materials can be additionally chemically or physically treated using well-established methods known from polymer science and technology (grafting by suitable species, plasma treatment, etc.) [14].

This review is focused on various aspects of tertiary treatment via granular deep-bed filtration. The importance of polymeric materials, as well as carbon nanostructures, which may be an alternative to the current media have been highlighting. The particular potential of polymers is based on their broad availability and low price (particularly for polyolefins), the simple treatment of their surfaces through a variety of chemical and physical methods to design surfaces with tailored surface free energy (wettability), and the porosity. Polymer technology offers a variety of well-established methods for designing foams with tailored porosity, which, together with appropriately tuned surface energy and controlled roughness, would open new avenues for the production of foamy media for efficient oil/water separation. Crucial inventions in deep-bed filtration is also involved in this paper.

2. Emulsions and Surfactants

An emulsion is a mixture of two or more mutually immiscible liquids, in which at least one of them forms a continual phase and the other occurs as a discrete phase, usually in the form of small droplets. The size of droplets is in the range from 0.1 to 10 μm , which relates to the range of visible light wavelengths [15].

2.1. Emulsion Instabilities

Tertiary treatment of wastewater often deals with emulsified oil in water. Hence, it is critical to identified type of created emulsions and their possible destabilization, which can dramatically increase efficiency of tertiary treatment process. This part will briefly summarize most occurring emulsions instabilities of oils in water [1].

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wavelengths [15]. Emulsions instabilities are important feature and contribute to separation process in deep-bed filtration. Emulsion instabilities can be generally divided into five groups, as shown in Figure 2 [16,17].

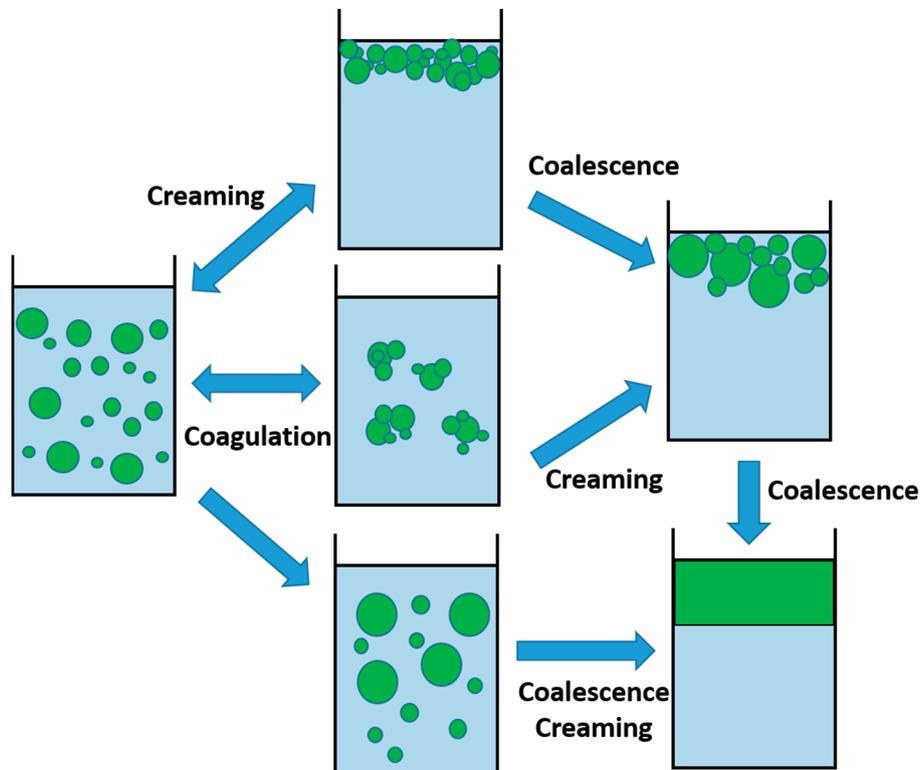


Figure 2. Schematic sketch of emulsion instabilities. Evolution between creaming, coagulation, coalescence.

2.1.1. Ostwald Ripening

This mechanism involves the diffusional transport of dispersed species from smaller to larger particles due to the differences in the Laplace pressure of nearby particles [16]. This process is governed by the pressure gradient, not by the concentration gradient. The Laplace pressure depends on the curvature of the species' surface, and spheres depend reciprocally on their radius. Therefore, this property enhances the solubility of smaller droplets and initiates an enlargement of larger particles through the merging of nearby small particles [16–18].

2.1.2. Creaming (or Flotation)

This phenomenon occurs due to unbalanced gravitational and buoyancy forces, accomplished by Stokes forces. If the droplet size is too small, Brownian motion and electrostatic forces influence a random movement of droplets more significantly, and droplets cannot float up to the surface. However, once droplets reach some critical size, the buoyancy force will be dominant, and droplets float to the surface of the liquid, where they form a layer from closely attached individual droplets or a continuous film [16,17].

2.1.3. Aggregation

Aggregation is a linking of a number of entities into a cluster. If the formation of aggregates is reversible, it is called flocculation; if it is irreversible, it is called coagulation [16,17]. Aggregation is common for the gelation of solid particles. In the oil/water separation process, aggregated oil droplets may represent a pre-stage before coalescence. The aggregation of droplets within the dispersing

medium is first explained by Brownian motion, which brings droplets into close contact. Once droplets are close to each other, the various inter-particle forces start to act, and depending on their magnitude, droplets will aggregate or not. There are two types of interaction forces: internal and external. The main internal attractive forces are van der Waals forces, particularly London dispersion forces [19]. This force tends to link nearby particles together. The forces that act against a linkage are repulsive electrostatic forces due to an equal electric charge on nearby droplets. A decrease in this repulsion force can be induced by the addition of acids (pH reduction) or ionic compounds, which increase the ionic strength of a continuous phase (water) [20]. The external forces are mainly hydrodynamic forces caused by the motion of liquid (stirring, shaking, flow) [19]. These forces are unfavorable for aggregation and, depending on their intensity, contribute to the disruption of formed aggregates.

2.1.4. Coalescence

Coalescence is a process in which individual droplets merge to form larger droplets, where an individual character of the original species is undistinguishable. Coalescence is more favorable if (i) the droplets are larger (and the size of the interfacial film between them is larger, meaning lateral dimensions), (ii) the film is thinner (attraction forces between droplets are stronger), and (iii) the oil/water interfacial tension is lower (the use of suitable surfactants) [19,20]. If these preconditions are fulfilled and an aggregate is stable for at least some time, the separating thin film can break due to Laplace pressure, and nearby droplets may fuse to form a larger droplet [19,20]. Coalescence is also promoted by extended contact time. This fact indicates that coalescence is not controlled merely by electrostatic interactions, which always act instantaneously, but also by diffusional processes. Coalescence mostly occurs at the interphase with the third phase, which is usually air on the top of the free water surface, or through de-emulsification initiated by either in situ-formed gas bubbles in an emulsion or a solid material surface (membranes, sorbents, coalescers) [21–25]. Solid surfaces can be modified by tailoring their surface tension and topology, which enables tuning of the contact time, shape of attached droplets, and inter-droplet distance, as will be discussed later. In particular, the most important factor is the character of the filter material in terms of its surface tension and topology (roughness and pore size) and the character of interactions at the interphase surface/emulsified droplets (oil) and surroundings (water) [21–25]. These phenomena govern the wetting of the solid phase by oil and the tendency to form spread films and attached droplets, which can coalesce and leave the surface in the form of larger droplets. Coalescence enhances the separation efficiency of the filter because the amount of a removed oil component is not given only by adsorption at the surface of the medium. The formation of large droplets within interstices of medium particles (so-called straining) significantly contributes to the separation efficiency [26]. On the other hand, straining leads to a decrease in the flux rate (pressure drop). Industrial filtration technologies use well-balanced processing conditions in terms of the height of the bed, size of the medium, and inlet flow, which enable cleaning of the deep-bed just once per 24 h, usually through backwashing [27]. More details about the mechanisms of coalescence, experimental techniques, and modeling can be found, for instance, in the review of Kamp et al. [28], and the theoretical aspects of emulsion stability are described in the chapter by Danov [29].

3. Oil Sorption Media

Oil adsorbents are materials that attract oil products preferably into their bulk, whereas adsorbents attract and coalesce the oil on the surface of the adsorbing material. Generally, adsorbents have better efficiency for thicker oils, while adsorbents are more effective with lighter oils [1]. Oil sorbents can be divided into natural (organic, inorganic) and synthetic sorbents. Natural oil sorbents have been used extensively in the past, most common are carbon based materials, lignocellulose materials, sand, nutshells, etc . . . [1] Oil sorbents based on synthetic materials, such as polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), nylon, polyethylene (PE), and other polymers, are able to attract oil while repelling water.

3.1. Natural Materials

Various natural materials have been used as oil absorbents for the removal of effluents such as heavy, crude and other types of oils accidentally spilled into the environment. These materials include straw, expanded perlite or coir dust. Carbon-based materials found in nature represent organic natural oil sorbents including corn cobs, walnut shells, sugarcane pulps or feathers. Natural materials, such as sand, volcanic ash or clay, which cannot be incinerated, are considered inorganic oil sorbents. In particular, the surface of coir dust contains an abundance of fine pores, which can be easily impregnated by hydrophobic materials, providing a desired water repellence and a high mineral oil absorptivity. The coir dust used for oil/water separation can consist of a mixture of materials with various irregular shapes such as lumps with dimensions of 8–10 mm, particles (5 mm) and fine powder particles (<1 mm), but preferably used are particles with dimensions of 0.5–3 mm and a specific gravity in the range of 0.05–0.1 g/mL [30].

The absorbance medium should comprise a random loosely arranged design containing voids that oil can be absorbed in. In practical aspects, a pore size range from 500–40,000 nm is effective for absorbing oil. It was found that a fine powder of charcoal ground to a size of less than 60 μm (destroyed voids and pores) did not significantly deteriorate the sorption capacity. However, smaller particles can absorb oil more rapidly than larger particles. This observation shows that absorption is not controlled by the capillary effect but rather by formation of an oil film on the charcoal surface with subsequent oily particle aggregation, which can be easily recovered. On the other hand, very fine charcoal powder is susceptible to an explosion hazard while stored in a closed environment. For this reason, the size of these particles is preferably less than 1 mm [31]. Charcoal is slightly hydrophobic, but after contact with water, the oil uptake is reduced because the voids inside are occupied by water [32]. Moreover, the specific gravity of void-free carbon is more than 1; therefore, charcoal has a tendency to sink in water prior to taking up oil.

Fumed silica treated with hexamethyldisilazane or octamethylcyclotetrasiloxane was invented for oil absorption from water without water absorption because of its hydrophobic character. The issue associated with using untreated amorphous silica is that it is concurrently both hydrophilic and oleophilic. The treated fumed silica is then able to selectively absorb hydrocarbons (benzene, toluene, tetrahydrofuran, methylethylketone, acrylic acids and high molecular weight alcohols) while ensuring water repellence. Moreover, this material can effectively absorb crude oil and its derived products such as diesel fuel, gasoline, heating and motor oil from oil-in-water and emulsions [33].

Natural lignocellulosic materials, such as kenaf cores, can be used as adsorption media for the physical removal of oil and other colloidal solids from wastewater. This material can be used in a multistep wastewater treatment process (primary, secondary, tertiary) or in each step to enhance the treatment process [34].

A few studies have been devoted to kapok as filter media for oil/water separation [35–37]. Kapok is a silky fiber that encloses the seeds of kapok trees (*Ceiba pentandra*). Kapok fiber is composed of single-celled plant hairs, in contrast to cotton, which is lignified and not attached to the seed grains. Kapok fiber-based materials have opened up possibilities for various new application fields, especially as absorption agents [38].

3.2. Nutshell Filters

Deep-bed media filters that constitute granular nutshells are termed “nutshell filters”, most commonly used in the tertiary treatment of produced water treatment. In the petroleum industry, nutshells have been the preferred media for producing water filters for over 40 years [39].

Over the years, several other materials have been explored for use in deep-bed filtration, including English walnut, pecan, coconut, apricot hull, and palm kernel, of which black walnut shell (*Juglans nigra* L.) has been deemed the best medium [40]. Ground walnut shells are hard, chemically inert, nontoxic and biodegradable [41]. This material is available in abundant supply as a byproduct of the walnut industry, making it a renewable resource. Walnut shells are hydrophilic, and they remove

oil by coalescing oil droplets [39]. Despite showing lower sorption capacity than other media, walnut shells are the continued choice in deep-bed filtration due to their coalescing nature, incompressibility and resistance to attrition. This material has a unique affinity for oil, which is strong enough to aid in adsorption but also weak enough to release the oil droplets during backwashing [42]. It is also mechanically tough enough to withstand the high pressure during the backwashing operation, thereby reducing possible loss of media during the subsequent backwashing cycles [43]. In addition, due to the lower density than that of alternative materials such as sand or garnet, less energy is required for fluidization and scrubbing [40].

Even though sand and anthracite have similar performance results to those of BWS, they have the following disadvantages. Sand is relatively heavy (requires higher backwash energy) and abrasive (reduces the lifetime of the media and filter components). Anthracite is easily fractured into relatively flat flaky particles (blinds off the filter prematurely) [40].

Natural materials, such as walnut shells, pecan hulls, and apricot pits used by themselves or in combination, have become preferable adsorbents for filtration because of their high sorption efficiency and easy backwashing process, which can be carried out directly within the vessel [41].

The walnut shell (English, black or other type) is the most industrially used filter medium in filtration apparatuses. Walnut shell media is known for its affinity for both oil and water (desirable filter media) and is commonly used for oil removal wastewater. The bed depth of the filter media can vary based on vessel requirements from 0.25–1.7 m and more. Any material can be used for the construction of the vessel, such as cement for open types and stainless steel, coated carbon steel or polymer reinforced by fiberglass for closed types of vessels.

Within the wastewater treatment industry, walnut shell media filters are widely used for oil removal due to their simplicity and low cost [40]. With advances in polymeric media, a superior performing and cost-effective product (or combination thereof) can be developed capable of removing the myriad of oil-containing compounds (dispersed hydrocarbons, fatty acids, emulsions) in wastewater. In comparison with advanced membrane processes, polymeric media filtration can be more easily adopted by the industry since operators are familiar with the technology basics and this reduces risk, a key element of any process or decision [44]. Studies devoted to oil/water sorption for natural materials is summarize in Table 2.

Table 2. Studies devoted to sorption materials based on natural materials.

Media	Oil/Water Mixture	Sorption Capacity	Inlet	Outlet	Reference
Charcoal	Hydrocarbons in water	10.90 mg/g	100 ppm	below 1 ppm	[32]
Silica	High molecular weight alcohols diesel fuel, gasoline, heating and motor oil water emulsions	10 g/g	N/A	below 1 ppm	[33]
Kapok	Vegetable oil or diesel polluted water	32.31 g/g	11,500–13,150 ppm	126	[37]
Kapok	diesel oil	N/A	2.5 wt.%	99%	[36]
Kapok	Diesel and hydraulic oil	N/A	5 to 15 wt.%	Over 99%	[35]
Sawdust	Metalworking fluid		3 wt.%	99%	[45]
Walnut shell	Mineral oil, vegetable oil, DoALL Bright-Edge oil,	0.56 to 0.74 g/g	N/A	N/A	[41]
Black walnut shell	Hydrocarbons	N/A	100 ppm	Below 5 ppm	[40]
Walnut granules	Hydrocarbons	N/A	50–100 ppm	2–5 ppm	[43]

3.3. Synthetic Materials Used for Oil Sorption in General

Useful materials for oil (petroleum- and vegetable-based) filtration from water can be in the form of sponges and foams of various kinds including PVC, PP, PS, PE, nylon, or polyvinyl chloride-vinyl acetate copolymers, but a preference is for hydrophobic polymers [46]. This foamy material is mainly used in specific forms, such as powdered, shredded, chopped, disintegrated, ground or granular forms. These absorbing materials can be modified by a hydrophobic residue consisting of decomposed

ammonium/amine salt by heating an aliphatic/cycloaliphatic carboxylic acid and oil to avoid the absorption of water [47].

The synthetic material absorbing oil can include particles (sorbent) with an average aspect ratio of approximately 5 to approximately 500 with an average particle diameter range of 10 μm to 1 mm. This material can comprise hydrophobic PP or PE fibers in the outer layer, inorganic fillers and hydrophilic absorbent core material (synthetic or natural fibers) [46]. Any shape of particles can be used in oil absorption, such as cubes, cylinders or sausages [48]. Jenkins [49] described the application of a homopolymerized acrylamide and its copolymers with a molecular weight of at least 40,000 but preferably up to 1 million to break up oil/water emulsions, which are effective for 10–50 ppm. Additionally, many efforts have been made to manufacture synthetic filter media. Essentially, all of those approaches utilize some form of thermoplastic material [50], such as PVC [51–53], PP [54], polytetrafluoroethylene [55], PE [53], nylon [56], and polyvinyl [57]. However, their relatively higher price than that of conventional inorganic filter media has limited their commercial utilization in filtration applications. Sand and anthracite were used for many years in filters, with satisfactory results. However, the use of filters including multilayered media provided better clarity of effluent with long filtration runs in deep-bed filter applications [58].

3.3.1. 3D Materials

Polymer foams and sponge-based materials have gained considerable interest due to their inherent properties such as easy availability, low cost, low weight to volume, extremely high porosity, tunable surface properties and high sorption capacity [59]. In addition to foams and sponges, other 3D porous materials such as aerogels and hydrogels exhibit great potential as adsorbents largely due to their well-developed pores and high surface area, which are known to enable extremely fast and selective adsorption of organic solvents and oils from water, with a high capacity [60].

Table 3 summarizes some studies performed on polymer foams and is not an exhaustive list by any means. The table is followed by a short explanation of the mentioned works.

3.3.2. Polyurethane (PU)

PU sponges are widely studied for their oil sorption capability because they are durable, inexpensive, easily available, and highly porous (high oil sorption capacity) and have excellent elastic properties, enabling them to recover to their initial state after many rounds of compression [60]. The only obstacle is that PU consists of several carbamate and amide groups, making it hydrophilic, which means that the material selectively uptakes not only oil but also water [60]. Therefore, surface modifications are required to achieve selective adsorption of oils via fine-tuning of the wetting properties. Several attempts have been made to make PU sponges hydrophobic for applications in oil/water separation. A technique commonly used for functionalization of PU foams is etching with acids such as dichromic acid and sulfuric acid, followed by chemical functionalization with low-energy molecules [60]. The drawback of this technique is the degradation of the PU backbone because of the acid used [20]. Therefore, other techniques that work by the application of external stimuli are more convenient and offer better control of the separation process.

Guselnikova et al. [59] employed a facile approach for the preparation of a recyclable superhydrophobic magnetic PU sponge with a high oil sorption capacity. To impart superhydrophobicity, the PU sponge was modified using 3,5-bis(trifluoromethyl)benzenediazonium tosylate. Next, the incorporation of hydrophobic magnetic nanoparticles modified by the same diazonium salt resulted in the formation of a functional magnetic material for the separation of oil- and organic solvent-containing wastes. The prepared sponge had a high sorption capacity, and it exhibited superhydrophobicity, with a WCA value of $168 \pm 1^\circ$. Li et al. [60] employed graft copolymerization to improve the oleophilic properties of PU foam for oil sorption. Copolymerization was performed using divinylbenzene as the cross-linker, benzoyl peroxide (BPO) as the initiator, and toluene as the solvent. The modified foam exhibited a maximum sorption capacity of 46.98 g for diesel and 41.42 g

for kerosene per gram of modified PU. In another attempt to improve the oil/water selectivity of PU foams, Wu et al. [61] treated PU sponges with silica sol and gasoline using a simple dip-coating approach. The prepared sponge exhibited a water contact angle of 126° and an oil contact angle of 0° . The authors attributed this transition from hydrophilicity to hydrophobicity to the increase in surface roughness due to the silica nanoparticles attached on the surface. Three types of oils were used to study the sorption capacity, namely, motor oil, peanut oil and diesel, with values determined to be 103 ± 3 , 108 ± 4 and 95 ± 3 g/g, respectively. The prepared sorbent could be regenerated using a simple mechanical squeezing process and reused more than 15 times. Su et al. [62] coated the inner surface of PU foam with a superhydrophobic nanosilica film to obtain a hydrophobic and oleophilic foam. The contact angle of the prepared foam was 152° for water and 8° for kerosene. The foam selectively absorbed kerosene from the kerosene–water mixture and could be regenerated just by drying at 30°C . Pan et al. [63] reported another approach to fabricate a superoleophilic and hydrophobic flexible PU foam (FPUF). They used a layer-by-layer self-assembly technique on a foam surface to alternately deposit positively charged chitosan and negatively charged titanate nanotubes on the foam surface, followed by modification with dodecyl mercaptan. The prepared foam exhibited a water contact angle of 128° and an oil contact angle of 0° . The hydrophobicity was attributed to surface roughness, and the superoleophilicity was claimed to be from dodecyl mercaptan. The oil sorption capacity recorded was 32 g/g for diesel and 30 g/g for soybean oil. The absorbed oils were collected by a simple mechanical squeezing process; the sorption capacity was constant for the first six cycles, after which it suffered a slight drop in capacity; and the authors claimed that the mechanical squeezing process caused the size of the foam to shrink, indicating reduced pore volume. Kong et al. [64] used hollow Al_2O_3 spheres to fabricate a hydrophobic and oleophilic PU foam. The hollow Al_2O_3 spheres were prepared by a one-pot hydrothermal method and modified with g-methacryloxypropyltrimethoxysilane. The hydrophobic and oleophilic polyurethane (Al_2O_3 /PUF) foam sponge was prepared using a foaming technique. The hydrophobicity, oil absorption capacity, and reusability of the Al_2O_3 /PUF foam sponge were tested. The results showed that the water contact angle of the modified PUF exceeded 140° , with the sorption capacity for chloroform being 37 g/g, and the modified foam was reusable for up to 10 cycles with no considerable loss in its absorption capacity.

3.3.3. Melamine Formaldehyde (MF)

The MF sponge is light, highly porous and robust having high nitrogen content and it is a flame retardant, which is favorable properties for an oil sorbent. However, similar to PU foams, MF sponges also suffer from poor oil selectivity. The manufacturing process of melamine sponges results in secondary amino groups, which are often used for modification [65].

Ruan et al. [65] used a commercially available low-cost MF sponge and made it superhydrophobic using a facile two-step strategy. The first step consisted of immersing the hydrophilic MF sponge in an aqueous solution of dopamine, which resulted in the deposition of a thin layer of polydopamine (PDA) film over the entire surface. Next, a single layer of hydrophobic molecules with low surface energy was grafted on the surface by immersing the PDA-coated sponge into a solution of mercapto-functionalized hydrophobic molecules. The resulting sponge exhibited excellent absorption performance, including a high absorption capacity and excellent selectivity. The modified sponge exhibited superhydrophobicity, with a water contact angle of 163° . Excellent oil sorption capacity was recorded for 100 g/g pump oil and 102 g/g soybean oil. The absorbed oils were easily recovered by mechanically squeezing the foam.

Table 3. Studies devoted to sorption materials based on polymeric foams.

Polymer	Treatment	Sorption Capacity (g/g)	Desorption Method	Water Contact Angle (°)	Pore Size (µm)	Reference
PU	Surface functionalization and introduction of magnetic nanoparticles	Chloroform: 77.2 Xylene: 58.3 Pump oil: 53.1	Mechanical squeezing	168	N/A	[59]
PU	Graft copolymerization	Diesel: 46.98 Kerosene: 41.42	Mechanical squeezing	N/A	N/A	[60]
PU	Surface treatment by immersion in SiO ₂ sol and subsequently gasoline	Motor oil: 103 Peanut oil: 108 Diesel: 95	Mechanical squeezing	126	N/A	[61]
PU	Superhydrophobic surface coating		Drying at 30 °C	152	N/A	[62]
PU	Layer-by-layer self-assembly of chitosan and titanate nanotubes	Diesel oil: 32 Soybean oil: 30	Mechanical squeezing	128	N/A	[63]
PU	Impregnation with Al ₂ O ₃	Chloroform: 39	Rinsing with ethanol, squeezing and drying	140	N/A	[64]
MF	Dip-coating and grafting	Pump oil: 100 Soybean oil: 102	Mechanical squeezing and solvent extraction	163	N/A	[65]
MF	Surface modification: Silica nanoparticle adsorption and silanization covering	Hexane: 60 Toluene: 77	Mechanical squeezing	N/A	N/A	[66]
MF	In situ synthesis of Fe ₃ O ₄ particles and dip coating of Candelilla wax (CW).	Cyclohexane: 55 Tetradecane: 104	Rinsing with ethanol and drying	158	N/A	[67]
MF	Impregnation with GO	Silicon oil: 54 Chloroform: 76.4 Liquid paraffin 45.2	Mechanical squeezing	130	N/A	[68]
PDMS	3D printing using sacrificial molds for precise control of pore size	Diesel: 800%	Rinsing with ethanol, squeezing and drying	143	400	[69]
Natural rubber foam	Vulcanization and cross-linking	Petrol: 7 Kerosene: 6 Diesel: 5.5	Mechanical squeezing	95	639	[70]
PS	Impregnation with oleic acid-coated Fe ₃ O ₄	Diesel oil: 14.41 Lubricating oil: 17.83	Mechanical squeezing	141	500	[71]
Poly(St-DVB)	Incorporating carbonyl iron powder to obtain a composite	Diesel oil: 22.7 Gasoline: 21.9	Centrifugation	142	N/A	[72]

Gao et al. [66] reported the two-step hydrophobic fabrication of a melamine sponge. SiO₂ nanoparticles were synthesized and anchored on the surface of the melamine sponge to increase the surface roughness of the sponge. The sponge was then dip-coated in a vinyltrimethoxysilane (VTMS) solution, and this step improved its hydrophobicity. The modified sponge was oleophilic and exhibited a high sorption capacity for a variety of oil/solvents (60–109 g/g). The sponge was subjected to the absorption-squeezing process to study its reusability potential, and it successfully retained its hydrophobicity, elasticity and oil absorbency after 12 cycles. Yin et al. [67] took inspiration from the waterproof mechanism of a small Candelilla shrub and produced a superhydrophobic magnetic melamine sponge via in situ synthesis of Fe₃O₄ and dip coating of Candelilla wax. A combination of the high porosity of the hierarchical structure and low surface energy resulted in the prepared sponge exhibiting hydrophobicity (WCA, 158.8°) and high oil selectivity. To regenerate the sponge, it was simply washed with ethanol and dried in the oven. Zhou et al. [68] used graphene oxide (GO) to modify a commercial melamine sponge. The group used silk fibroin (SF) protein, a commonly used natural protein biomaterial that is biocompatible and biodegradable [28], to combine MS and GO. Due to its porous structure and hydrophobic nature, the prepared foam had excellent oil adsorption capacity

(silicon oil: 54 g/g, turpentine: 50.1 g/g, liquid paraffin: 45.2 g/g), excellent mechanical properties, and superior recyclability, and it can be used up to 50 times.

3.3.4. Polydimethylsiloxane (PDMS)

PDMS is an inexpensive, biocompatible, flexible, chemically and mechanically strong polymer. It is naturally hydrophobic and hence can selectively absorb oils and organic solvents from contaminated water [69]. Further, reusability can be easily achieved by simply squeezing PDMS sponges. 3D printing has the potential to allow control of a sponge's inner architecture, providing substantial benefits. Shin et al. [69] used 3D printing to prepare PDMS sponges with improved absorption capacities, intended for oil–water separation. Templates with a well-ordered porous architecture were printed using polycaprolactone (PCL). The obtained sponges were characterized and found to be hydrophobic and oleophilic, with water and oil contact angles of 100–143° and ~0°, respectively. For diesel, the nonhollow and conventional PDMS sponges had absorption capacities of approximately 100–350% and 600%, respectively, and the bioinspired hollow PDMS sponge showed the largest sorption capacity value, approximately 800%.

3.3.5. Natural Rubber

Natural rubber is a low-cost material; it is a type of polyisoprene and is classified as an elastomer [70]. This material is waterproof and resilient, with a high stretch ratio, and it has good resistance against aging and weather.

Lazim et al. [70] prepared a new macroporous and oleophilic natural rubber (NR) foam by using the vulcanization process. They used methanol as the solvent and varying amounts of disulfur dichloride, a cross-linking agent. This work was the first to report the preparation of a sponge-like foam made of LNR, which had an interconnected open-cell structure with a pore volume ranging from 1.83 mL/g to 4.28 mL/g and diameters between 2.09 µm and 13.24 µm. The sorption capacity of LNR-foam was found to be similar to that of cotton fiber-based sorbents, with a sorption capacity of up to 9.39 g/g for most oils. The prepared LNR foam had a water contact angle of 95.8°. The reusability test indicated that the performance of LNR-foams remained unchanged for up to 20 absorption cycles, demonstrating good reusability, with approximately 90% of absorbed oil being recovered by mechanical squeezing.

3.3.6. Polystyrene (PS)

Yu et al. [71] successfully fabricated a strong magnetic polystyrene foam that withstood compression, showed good oil absorption capacity and was reusable. They reported the preparation of oleic acid-coated magnetic Fe₃O₄ particles, which were introduced into the foam using the ultrasonic dispersion method, resulting in a highly hydrophobic magnetic polystyrene foam. The incorporation of Fe₃O₄ particles or oleic acid-Fe₃O₄ particles allowed the oil-absorbing foam to be easily extracted using a magnetic field. The oil sorbed by the foam could be recovered using simple mechanical squeezing. The sorption capacities of OA-MPF for diesel oil, lubricating oil, DMF, and octane were 14.4, 17.8, 13.6 and 14.4 g/g, respectively.

3.3.7. Poly(styrene-divinylbenzene)

Zhang et al. [72] also fabricated a magnetic foam by employing carbonyl iron powders. A technique called high internal phase emulsions (HIPEs) was used to prepare a foam with a highly open porous structure, resulting in a foam with 98.1% porosity. The prepared foam exhibited a water contact angle of 142° and excellent oil selectivity. It had an oil sorption capacity of 22–23 g/g for diesel and gasoline. Additionally, the magnetic foam could be easily extracted using a magnet. The saturated foam could be regenerated by using centrifugation, and the foam maintained its oil uptake capacity even after 10 absorption/regeneration cycles.

3.3.8. Carbon-Based Foams

Carbon-based absorbents have great potential as oil sorbents since they possess a high surface area, low density, excellent mechanical properties, good chemical stability, environmental friendliness and a large pore volume [73–76]. Various carbon nanotube (CNT)-based materials have been engineered to be superhydrophobic oil sorbents owing to their intrinsic nanotextured and porous architectures with superwetting surface properties [77]. CNT-based oil sorbents have undergone a revolution in design from individual nanotubes to recently engineered three-dimensional (3D) aerogel/sponge-based CNT materials [78]. 3D CNT aerogel/sponge sorbents offer numerous advantages over powdery nanotube sorbents, including ultralight weight (low density), inherent superhydrophobicity/oleophilicity, strong chemical/mechanical properties, large surface areas, tunable porosity, and reusability. A summary of the selected properties of carbon-based foams is provided in Table 4.

Gui et al. [79] used chemical vapor deposition (CVD) to fabricate a sponge composed of self-assembled, interconnected CNT skeletons. The prepared sponge had an impressively low density of 5–10 mg/cm³ and a porosity of >99%. It also boasted excellent structural flexibility and could be deformed elastically and compressed to large strains repeatedly in air or liquids without degradation in structure. The foam had a high absorption capacity for a wide range of solvents, showing absorption capacities as high as 180 times its own weight. It was hydrophobic in nature, with a WCA of 156°, and could be regenerated by simple mechanical compression.

In another work by the same group [80], the researchers prepared magnetic CNT sponges using CVD. The magnetic sponges showed a sorption capacity of 56 g/g for diesel and excellent reusability potential (more than 1000 times). The density of the magnetic carbon nanotube sponge was 15 mg/cm³, with a WCA of 140°.

3.3.9. Graphene-Based Sorbents

Graphene aerogels, fabricated by different approaches including solvent exchange followed by freeze-drying, hydrothermal cross-linking and polymerization, freeze-drying, heating in an oil bath followed by a chemical reaction vessel and freeze drying, etc., have shown great potential in the field of oil spill cleanup due to their ultra-lightness, high compressibility, tremendous porosity and high specific surface area [81].

Bi et al. [81] reported for the first time the preparation of “spongy graphene” (SG). It was fabricated by reducing graphene oxide (GO) platelets in suspension followed by shaping via molding. SG was tested for its sorption capacity without any further modification and showed an absorption efficiency of 20–86 g/g for a variety of solvents and oils. SG exhibited a water contact angle of 144° and could be regenerated by heating and reused more than 10 times with no change in its sorption efficiency. Li et al. [82] prepared a compressible and fire-resistant graphene aerogel by employing one-step reduction and self-assembly of GO with ethylenediamine, followed by freeze-drying. The obtained aerogel was light, with a density in the range of 4.4–7.9 mg/cm³ and porosity up to 99.6%. With a WCA of 155°, the aerogel exhibited a faster absorption rate (27 g/g/s) than pure graphene. The aerogel was able to absorb different organic liquids, with a sorption capacity varying from 100 to 250 g/g depending on the density of the organic liquids. Zhao et al. [83] prepared an ultralight, nitrogen-doped, three-dimensional graphene framework (GF). The prepared aerogel showed a self-assembled, porous, interconnected, three-dimensional framework with an ultralow density of 2.1 ± 0.3 mg/cm³, which is similar to the density of air (1.2 mg/cm³) at room temperature. This ultralow density was attributed to its open pore structure. The GF showed an absorption rate of 41.7 g/g/s for gasoline, which is higher than the previously reported sorption rate for pure graphene and graphene aerogels. It also showed very high absorption capacity, 200–600 times its own weight for different oils and organic solvents. This GF was also able to withstand relatively large deformations (e.g., 60%) under manual compression and elastically recover to its initial volume. Gao et al. [84] fabricated reduced graphene oxide foam using three different freeze-drying methods. These foams were then tested for their sorption capacity using a variety of oils. The sorption capacity was in the order of olive oil > pump oil > lubricating oil > diesel oil > gasoline.

The sorption capacity for all the oils was higher than 100 g/g with a maximum value of approximately 122 g/g for olive oil.

3.3.10. Carbon Aerogels

To date, pyrolysis of biomass is considered to be the simplest approach to produce carbon materials, as it is an inexpensive, sustainable, green preparation process, and the as-prepared materials are biocompatible and biodegradable [85].

Li et al. [85] prepared a three-dimensional carbon aerogel through pyrolysis of winter melon. The carbon aerogel had a high hydrophobicity density of 48 mg/cm³, with a water contact angle of 135° and selective absorption for organic solvents and oils. The absorption capacity of the carbon aerogel for organic solvents and oils was 16–50 times its own weight. The material had a pore size of approximately 200 µm and a porosity of more than 97.5%, which is only slightly lower than those of CNT and graphene aerogels (99–99.5%). Its sorption capacity was investigated for gasoline, diesel and crude oil and was found to be 24, 27, and 25 g/g, respectively. In another attempt to prepare carbon aerogels, Wu et al. [86] employed freeze-drying followed by pyrolysis. The CNF aerogel showed an ultralow density of 4–6 mg/cm³ and a contact angle of 128°. The sorption capacity of the aerogel was tested for organic pollutants and oils and was found to be as high as 106–312 times its own weight. The material can be regenerated by distillation and direct combustion in air.

In addition to pyrolysis of biomass, other techniques and materials have been reported to synthesize carbon aerogels. Wu et al. [87] fabricated carbon nanofiber aerogels from macroscopic-scale synthesized carbonaceous nanofiber hydrogels using a template-directed hydrothermal carbonization method followed by freeze drying and pyrolysis. The prepared CNF aerogels had a self-assembled, interconnected, three-dimensional (3D) network structure with a very low density of 10 mg/cm⁻³ and a high porosity of 99%, consisting of both micropores and macropores. The aerogels also exhibited surface hydrophobicity, with a water CA of 135°. To demonstrate the sorption ability of these CNF aerogels, the sorption capacities for different commercial petroleum products including gasoline, diesel oil and pump oil were studied; the sorption capacity was found to be 61.14, 74.82, and 86.34 g/g, respectively. The CNF aerogel could be regenerated by heating or direct combustion in air.

Graphene and CNT aerogels have shown good absorption capacity and reusability because of their low density, high aspect ratio, good elasticity and excellent mechanical properties. Some works went a step further and combined the two materials to prepare hybrids [88]. Hu et al. [88] prepared a multiwalled carbon nanotube (MWCNT)–graphene hybrid aerogel showed superhydrophobicity and superoleophilicity. The sorption capacity was tested using a variety of oils, and the results were as follows: pump oil, 138 g/g; diesel, 120 g/g; and gasoline, 110 g/g. Desorption was performed by mechanically squeezing the aerogel, which was able to survive 90% compression and recover to its original volume upon removal of the external force.

Dong et al. [89] used a two-step CVD process to prepare a highly flexible superhydrophobic 3D graphene–CNT hybrid foam. The hybrid material exhibited a water contact angle of 152.3° and an oil absorption capacity of 80–130 times its own weight. Similar to previous work, this group also related the sorption capacity to the density, viscosity and surface tension of the liquid being tested.

Sun et al. [90] developed a template-free, synergistic assembly strategy for the fabrication of ultralight 3D aerogels with controlled densities. The authors used graphene oxide and CNTs to prepare ultralight weight aerogels by freeze-drying aqueous solutions of CNTs and giant graphene oxide. It boasted ultralow density (0.75 mg/cm³), excellent porosity (99.9%), hydrophobicity (WCA ≈ 132.9°), an average pore size of 123 nm and extremely high absorption capacities (215–913 g/g) for oils and organic liquids. The aerogel also had good mechanical properties and exhibited nearly complete recovery after 50–82% compression.

Table 4. Selected properties of carbon-based foams.

	Preparation Method	Density (mg/cm ³)	Sorption Capacity (g/g)	Absorption Rate (g ⁻¹ s ⁻¹)	WCA (°)	Porosity	Pore Size	Desorption	Reference
CNT sponge	Chemical vapor deposition (CVD)	5–10	Diesel: 140	N/A	156	N/A	80 nm	Mechanical compression	[79]
Magnetic CNT sponge	CVD	15	Diesel: 56 Gas oil: 49	N/A	140	99%	N/A	Heat treatment	[80]
Graphene sponge	Shape molding	12 ± 5	Lubricating oil: 68.5	Dodecane: 0.57	114	N/A	N/A	Heat treatment	[81]
Graphene aerogel	Freeze-drying	4.4–7.9	CCl ₄ : 250	27	150	99.6%	50 µm	Mechanical compression	[82]
Nitrogen-doped graphene framework	Freeze-drying and annealing	2.1 ± 0.3	Gasoline: 600	41.7	N/A	N/A	N/A	Direct combustion in air	[83]
Reduced graphene oxide foam	Freeze-drying	N/A	Diesel oil: 110 Pump oil: 118	N/A	135	N/A	50 µm	Heat treatment	[84]
Carbon aerogel	Pyrolysis of winter melon	48	16–50	N/A	135	97.5%	200 µm	Distillation	[85]
Carbon aerogel	Pyrolysis of bacterial cellulose	4–6	106–312	N/A	128	99.7%	N/A	Direct combustion in air	[86]
Carbon aerogel	Freeze-drying and pyrolysis	10	Gasoline: 61.14 Diesel oil: 74.82 Pump oil: 86.34	N/A	135	99%	N/A	Drying or direct combustion	[87]
CNT-Graphene hybrid aerogel	Microwave irradiation	N/A	Pump oil: 138 Diesel: 120 Gasoline: 110	N/A	>150	99%	N/A	Mechanical compression	[88]
CNT-Graphene hybrid 3D foam	CVD	6.92	Compressor oil: 90 Sesame oil: 105	N/A	152	N/A	N/A	Oven drying	[89]
Carbon aerogel	Cryodessication	0.75	Crude oil: 289 Motor oil: 341 Vegetable oil: 41	Toluene: 68.8	132.9	99.9%	123 nm	Mechanical extrusion or heating	[90]

4. Laboratory Setups for Testing Oil/Water Deep-Bed Filtration

The filtration process for deep-bed filtration consists of the initial and transient stages [91]. In the initial stage, particle deposition occurs onto a clean filter; hence, particles are directly deposited onto filter grains, which has a negligible effect on the properties of the filter. The transient stage consisting of the ripening stage, working stage and breakthrough stage occurs after the initial stage and describes the remainder of the filtration process. The ripening stage is characterized by an improvement in the filter effluent quality over time or a decrease in the ratio of the effluent concentration to influent concentration. The working stage, in which particle removal remains essentially constant, generally follows the ripening stage. Finally, the breakthrough stage generally occurs in the later part of filtration, where the filter efficiency decreases with time. A decrease in the working pressure or/and an increase in the turbidity of the eluent are signs of initiation of the breakthrough stage, and washing of the media by backwashing needs to be executed [91].

The filters for deep-bed filtration usually operate over 20 h before attaining turbidity breakthrough, and they need to undergo a cleaning procedure via air and water backwash [91]. Backwash, usually performed for up to 20 min, will clean and prepare filtration media for another filtration operation. With the exception of a few unusual designs, rapid filters are washed by an upflow of water through the media, which carries away the deposits from the filter pores. In most cases, this flushing is preceded by some agitation of the media to scrub off the adhering deposits [91,92]. All these factors need to be taken into consideration while assembling a setup for deep-bed filtration in either the laboratory or the industry scale.

This section will provide brief overview of laboratory scale setups for various media and wastewater. Results of laboratory scale is often translated to industrial application as it provides fundamental foundation for implementation new media to large scale operation.

The typical setup (Figure 3) for deep-bed filtration to treat wastewater consists of feed tanks, a filtration bed with valves, a pump to gain the required pressure in the vessel, collector tanks for filtrate and impurity retention after backwash [92].

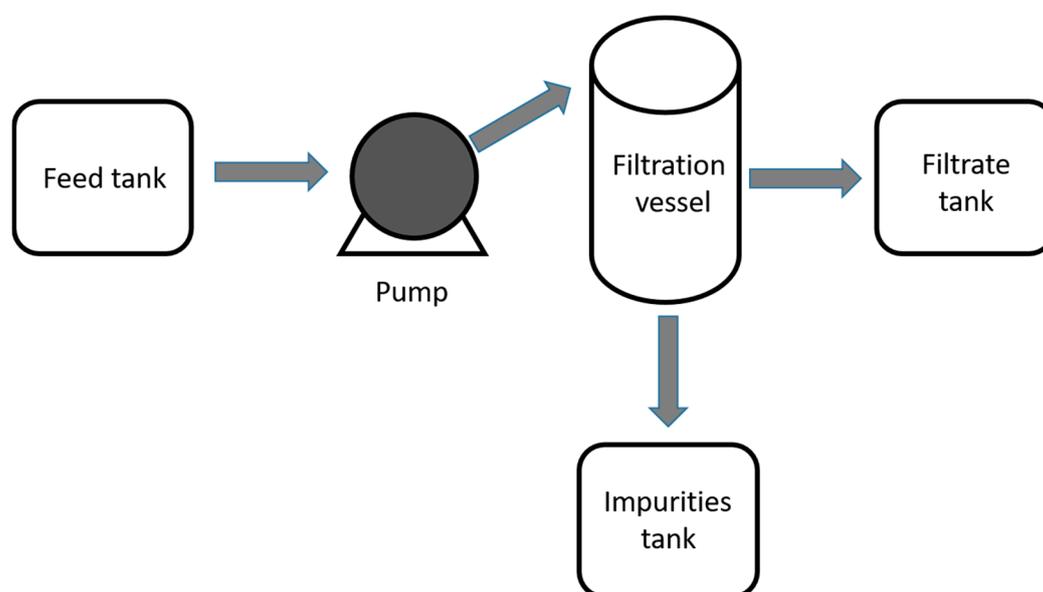


Figure 3. Schematic setup of laboratory filtration unit for separation of oil from oil/water mixture.

The core of the filtration unit is the filtration bed, which is in the form of columns of various lengths and diameters based on polymer [45,92,93], glass [35,36] or metal [94]. The common shape of the vessel for the filtration bed is cylindrical, and a metallic material is usually utilized [37,43,95].

A 10-cm-long glass column with an internal diameter of 2.71 cm and a bed volume of 57.68 cm³ packed by kapok fibers has been used for the separation of diesel and hydraulic oil mixtures at higher concentrations, from 5 to 15 wt.% of oil in water [35]. The oily waters were drawn into the kapok filter with a constant vacuum pressure of 12.57 kPa. Both the bottom and top ends of the column were covered with 1-mm perforated disks in order to distribute the liquid uniformly. It has been pointed out that oil retained in the filter can be recovered easily for reuse by a mechanical press while the wetted kapok can be reused, thus decreasing the cost of oily water treatment. A similar setup was used to study untreated and solvent-treated kapok media for deep-bed filtration of 2.5 wt.% diesel oil in water. With both untreated and solvent-treated kapok, greater than 99% of the diesel oil present in the 2.5% diesel/water influent could be removed by this deep-bed filtration system [36]. Another work [37] utilized kapok filter media for deep-bed filtration of 11.5 to 13.2 g/L oil and tap water, which was separately poured into tanks and carried the liquids toward the sieve. The water blended with oil was sprayed at a constant load through the sieve to filter the column. Afterwards, the water was collected in a container, and disk-like kapok fiber pads were used to absorb floated oil from the collected water. The kapok pads were then placed in a room environment for 24 h, allowing the evaporation of adsorbed water on the pad surfaces. Kapok shows potential as an effective filtering material for recycling oil from heavy oil-contaminated waters. However, the studies that utilized kapok filters for deep-bed filtration were focused on relatively high concentrations of oil in water contamination, from 2.5 to 15 wt.% of oil in water.

A 1.5 L cylindrical acrylic reactor filled with regranulated cork filter media was fabricated to filter refined sunflower oil wastewater at a concentration of 200 ppm in continuous mode. A 10-L agitated tank was filled with a raw emulsion that was fed to the reactor at a flow rate of 10 mL/min by a peristaltic pump. This setup achieved a decrease in the concentration of oil from 200 ppm to below 15 ppm.

Filtration experiments of different oils including crude oil, gasoline, diesel oil, and motor oil prepared by mixing oil and water using a laboratory mixer operating at 1000 rpm have been studied [45]. Filtration experiments were performed at room temperature by pumping oily water from a 2 L container through the sunflower pith filter bed in a downflow direction with a peristaltic pump. The column performance was studied at different initial oil concentrations (0.1 to 20 g/L), effluent pH values (4–10), flow ratios (5–30 mL/min) and bed heights (10–50 cm). However, sunflower pith media was able to remove only a limited quantity of oil, which indicates that this media is not suitable for the tertiary treatment of wastewater.

Rawlins et al. [92] studied walnut shell and pecan media for deep-bed filtration of 4-inch-diameter, 48-inch-long PVC columns packed by nutshell filter granular media held by mesh with inlet and outlet lines. Water and crude oil were sourced from separate tanks and injected into a filtration column through a static mixer. One aim was to investigate process parameters such as the type of media and flux salinity while obtaining an oil concentration at the outlet of below 5 ppmv. The authors found the maximum flux to ensure that the outlet oil concentration was below 5 ppmv. Full breakthrough of the media was estimated after 20 h of operation with a 100 ppmv inlet concentration of oil and after 30 h of operation with a 50 ppmv inlet concentration of oil, suggesting that backwash is recommended once a day.

A laboratory setups used for oil/water separation through deep-bed filtration are summarize in Table 5.

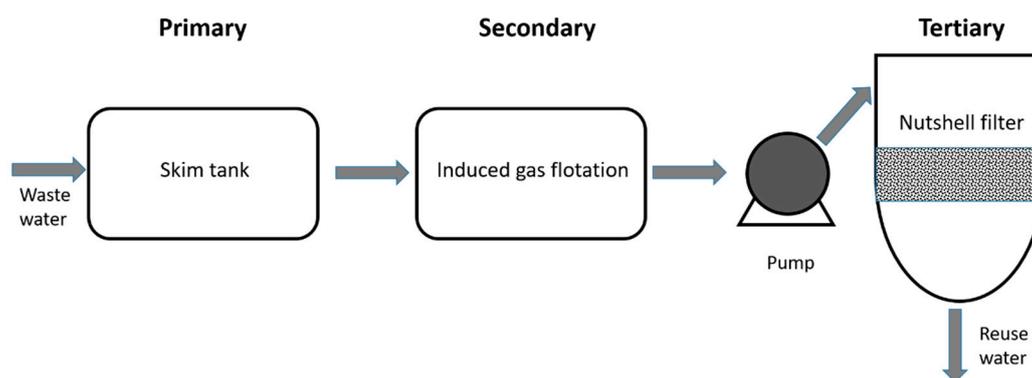
Table 5. Summary of laboratory setups used for oil/water separation through deep-bed filtration.

Bed Setup	Media	Oil/Water Mixture	Efficiency	Flow of Oil/Water Mixture	Reference
10-cm-long glass column, internal diameter 2.71 cm, volume 57.68 cm ³	kapok	5 to 15 wt.% diesel and hydraulic oil mixtures in water	99%	12.57 kPa	[35]
10-cm-long glass column, internal diameter 2.71 cm, volume 57.68 cm ³	kapok	11.5 to 13.2 g/L vegetable oil or diesel and tap water	99%	sprayed	[37]
1.5 L cylindrical acrylic reactor	regranulated cork	200 ppm refined sunflower oil wastewater	Below 15 ppm	flow rate of 10 mL/min by a peristaltic pump	[95]
2 L container	sunflower pith	crude oil, gasoline, diesel oil, and motor oil (0.1 to 20 g/L)	80%	downflow direction with a peristaltic pump	[45]
Phar-macia Biotech column model XK26/20, 0.2 m long	Sawdust	3 vol.% cutting oil	99%	0.5 bar	[92]
4-inch-diameter, 48-inch-long PVC column	walnut shell and pecan media	50–100 ppm crude oil	Below 5 ppm	peristaltic pump	[91]

5. Industrial Setups for Testing Oil/Water Deep-Bed Filtration

Industrial technologies for oil/water deep-bed filtration utilize various media such as sand, carbon type materials, polymers, nutshells, etc . . . choosing specific media rely on wastewater composition, requirement for final filtrate quality and other operation requirements [92].

Figure 4 shows an example of onshore treatment plant. Primary treatment is executed by skim tank where concentration of oil is lowering from few thousand ppm to approximately 500 ppm, followed by secondary treatment reduces oil content below 100 ppm by using induced gas flotation. Then, tertiary treatment is performed via deep-bed filtration by using appropriate media filter, often nutshell filters [92].

**Figure 4.** Nutshell filter arrangement for an onshore produce-water treatment plant [92].

Traditional deep-bed filtration utilizes porous media, such as sand or anthracite, with particle diameters in ranging from 0.5 to 0.8 mm. The drawback of such large particles is that a relatively deep-bed is required for effective filtration. In addition, back-flushing or backwashing of heavy sand particles is not effective since conventional approaches performed by efficiently flowing liquid through filter media do not intermingle and turn over media particles [96]. Any practical filter medium should have a density below 1.55 g/L as well as a high elastic modulus (over 40,000 psi) and should be nonabrasive [96]. Several synthetic polymers that meet these requirements fail in terms of industrial applications because they are expensive [97]. Some effort has been spent to develop dual or multi-type

media to overcome disadvantages in industrial scale applications such as plugging caused by high solid loading. Dual-media filter systems can handle high loading of impurities while operating at high filtration rates. In the past, conventional dual-media filter systems consisted of one or more layers made of anthracite coal with a specific gravity of 1.48–1.65 g/cm³ and a silica sand layer with a specific gravity of 2.65 g/cm³. The differences in specific gravity are responsible for the 2–3 times higher average particle size of the anthracite than of the sand; therefore, the backwashing process will not affect the arrangement of particular layers, while the anthracite layer will remain above the sand layer. A reverse-gradation bed using silica sand, crushed limestone or metallic materials (core) coated with a thermoplastic polymer (PE, PP, PVC, nylon, acrylonitrile butadiene styrene, polytri(or tetra)fluoro ethylene) with the same thickness as the core material and a specific gravity less than one has been studied [98]. These particles have outside diameters of 0.13–3.18 mm, ensuring gradient removal from the fluid, while the core particles have almost the same size in order to ensure proper specific gravity by changing the thickness of the outer coating. Different particle sizes and specific gravity allow gradual self-arrangement. This particle arrangement increases the efficiency of contaminant removal compared with conventional bed filters containing mixed particle sizes.

Rice et al. disclosed [99] a filter bed consisting of three different filter media particles with different sizes and specific gravities. These media were intermixed in terms of increased particle number alongside filtered fluid flow. The following media could be used: magnetite, ilmenite, garnet, tabular alumina, graphitic rock, and anthracite coal.

A filter medium made of irregular PVC particles significantly outperforms a sand filter [52], with the ability to obtain effluent with very low turbidity (approximately 0.2 ppm by 6 cycles). PVC, along with PE, or wood sawdust have desirable properties for being effective media in oil/water separation because of their lightness and great strength, making them stable for being backwashed utilizing mechanical and hydraulic forces [53].

Hirs disclosed a deep-bed filter consisting of several layers consisting of cylindrical polymeric particles based on nylon anthracite particles and sand [56]. This configuration enhanced contaminant filtration, ensuring that the pressure drop was minimized through the filter, which is crucial for industrial filtration applications.

Biomaterials, mainly nutshells, have all desirable properties and are water and oil resistant, do not deteriorate over extended time periods and are chemically stable [100]. In particular, black walnut shell filter media excel in the separation of oil from water while significantly outperforming sand or multimedia filters [100]. These walnut shell materials were invented in the oil industry in the early 1970s, and since then, they have undergone many innovations and evolutions. Benchmarked granulated black walnut shells possess the capability of coalescing oil from contaminated liquid flow and accumulating coalesced oil in the interstices of the filter media bed [100]. Water-saturated black walnut shells also exhibit a relatively weak affinity for oil, enabling rejuvenation of the bed by conventional backwash cycles. There are significant economic benefits that make black walnut shell media good candidates for use as filter media, such as commercial availability, elimination of medium treatment with solvents or surfactants, ease of removing accumulated oil and solids from the medium, reusability and very low attrition rate [100]. Today, walnut shell filtration is widely accepted for polishing oily water in upstream oilfield, downstream refinery and power plant facilities. With almost forty years of operational history, black walnut shells have been proven to be the best filter media material for simultaneous oil and solid removal from wastewater [92]. Backwashing of filter media is a crucial step that determines efficient deep-bed filtration. If no sufficient backwash is applied, media particles can agglomerate since the oil is not absorbed by the media. This process is called mud balling [101]. Conventional backwash systems include mechanical mixing and mechanical scrubbing with impellers and recycle lines, introducing high-velocity gas or water in the counter-current direction. These systems create dead spots that backwashing does not effectively reach, hence leaving oil within the filtration bed [43]. Several measures indicate the necessity of backwash, such as filtered water outlet quality, pressure drop across the filter and filtration time [92].

Backwashing can be performed inside the filtration vessel or in a separate scrubber vessel with media fluidized and pumped back and forth every cycle between two vessels. There are some requirements for proper backwash systems such as complete fluidization of the filter media bed, removal of trapped oil and solid particles, low stress and shear to the media granules, low water throughput, short cycle time, and low energy input [97].

During the last 60 years, several improvements in deep-bed filtration have been invented. Most of them rely on backwash systems to minimize water consumption and energy cost while successfully cleaning media filters. The following paragraphs will describe in more detail a summary of the most important inventions made in the development of deep-bed filtration. In 1969, Hirs et al. patented a method and apparatus for filtering [96] and rejuvenating granular bed media, where granular beds consist of PVC, PE, PS, sawdust or similar type material. Their invention provides a filter medium cleaning technique wherein a dirty filter bed of filter medium granules containing dirt from the filtration process is formed into a slurry and flowed past a perforated screen. The perforated screen has an opening smaller than medium granules; therefore, only liquid and dirt can pass through. Further improvement focusing on the filtration of small particles has been patented [97]. An introduction of permeable retainers on both the inlet and outlet sides of the vessel has also been proposed. In addition, contraction of the media bed by pressure leads to reduced void size; hence, increasing the effectiveness of entrapping small particles has been advised.

Further development of deep-bed filtration of oil in water mixtures led to the invention of first-generation black walnut shell deep-bed filtration [39], with the backwash consisting of an external scrubber with a pump, single backwash entry nozzle, backwash nozzle submerged in bed and side entry and nonmechanical liquid fluidization. However, several drawbacks made this technology unsatisfactory. One drawback was the requirement of additional space and cost due to external equipment such as a scrubber, piping, pump and valves. Another drawback was the inability to check for the sufficient removal and scrubbing of media. The major drawback comes from the presence of a stagnant zone below the filter bottom screen, which results in the mud balling effect. During the backwashing stage, the slurry of agitated media is pumped out of the main filter vessel from a top nozzle and sent through an externally located scrubber vessel where shell particles undergo intensive scrubbing along the scrubber screen tube. Contaminant-rich water streams flow through this screen and cleaned media particles are pumped back to the main filter vessel. Another drawback of this design is that the media settling in the scrubber vessel blocks the piping. This issue was addressed in next-generation deep-bed filtration technology.

Second-generation bed filtration technology changed the placement of the clean media return nozzle above the media bed level in the filter vessel, which prevented unnecessary media bed agitation during the media settling stage while still circulating the slurry through the scrubber vessel. This improvement resolved the uneven settling of the filtration bed that was observed in the previous generation [102]. This design change also allowed the reduction of media particles being trapped in the external scrubber. However, a number of disadvantages described in the first generation still prevailed.

The design of third-generation bed filtration technology includes an internal scrubber with a pump, a single backwash entry nozzle, a backwash nozzle above the bed and top entry and nonmechanical liquid fluidization [102]. An advantage of this design is that the scrubber vessel was eliminated, and the scrubber screen was placed inside the filtration vessel. This simplification prevents a medium from being trapped in the scrubbing vessel or piping, which overcomes the main drawback of first- and second-generation deep-bed filtration technology. However, some issues have not yet been resolved, such as costly motors required to pump the slurry through the scrubber vessel, requirement of a slurry pump, rapid attrition of the filter media resulting in excessive rate of media replacement and stagnant zone at the filter bottom and adjacent to the vessel shell resulting in the mud balling effect.

Fourth-generation deep-bed filtration technology brought outstanding improvement that eliminated the need for media to leave the vessel and to pass through the slurry pump [101]. Because the enhanced energy for fluidization comes primarily from a mechanical rather than fluid source,

this design has eliminated the mud balling stagnant zones from prior designs while simultaneously reducing the volume of water required for a backwash [101]. Backwashing takes place inside the main vessel, which significantly reduces the capital costs and overall footprint. The added mixer sufficiently agitates the filter media during the backwash stage, requiring less water than the previous design generations.

All described technologies so far have been invented to be used in horizontal setup deep-bed filtration. Next, the fifth generation was primarily invented for high-flow horizontally oriented setups [103]. This design eliminates all rotating equipment by using a multiphase gas/liquid backwash feed. The buoyancy of the gas carried on the high-velocity water jet creates a powerful fluidization force on the media while requiring a low volume of water, equal to that of the previous generation [103]. Each multiphase backwash jet fluidized a four-foot diameter zone of bed, and by networking into a header, very large filters were efficiently fluidized, with no dead zones and no rotating equipment or mechanical seals.

Having backwashing dependent on a particular filtration vessel possesses limitations because wastewater at the inlet needs to be temporarily blocked due to the backwashing cycle, which can potentially lead to damage to the inlet pump that continues to run dead headed, while fluid is prevented from passing through [104]. This limitation can be overcome by having a backwashing unit outside of the filtration vessels, which means easy access to the backwash system in the case of maintenance of the feed filtration vessel. An interesting approach combines multiple filtration vessels, each of which utilizes a common backwash unit located exteriorly from filtration units. Multiple tank setups allow the continuous operation of wastewater treatment, which allows tailoring daily run capacity and protecting pumps, which do not need to run as discontinuous processes due to backwashing or possible maintenance of the filtration tank.

An example design with an external pump and internal screen [92] is shown in Figure 5. In filtration mode, valves A and E are open, allowing continuous downflow of the water through the media bed. Oil and solids are captured by the media and accumulate within the bed depth. Contaminant buildup increases resistance to flow, indicated by a corresponding increase in the pressure drop. If the pressure drop becomes too high, then fluid channeling or bypass will occur, allowing oil to reach the outlet. A preset pressure drop alarm indicates the need to clean the media bed. During backwash, the filter is taken offline (valves A and E are closed), and a standby filter is brought online to allow continuous water treatment in the plant.

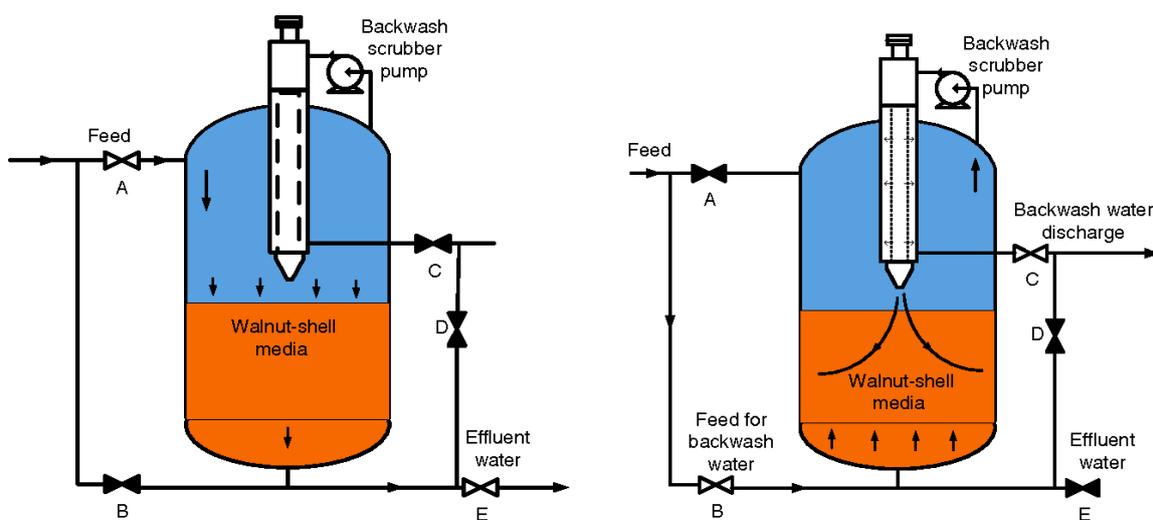


Figure 5. Typical nutshell-media technology operation during (left) filtration and (right) backwash cycles [95].

In the example shown in Figure 5 Right, feed water is first used to fluidize the media bed by opening valve B. The scrubber pump draws in the fluidized dirty media, wherein oil is scrubbed off via shearing as it passes through the pump. The mixture is returned to the filter body by passing through a cylindrical screen enclosed in a pipe. The removed contaminants (oil and small solids) pass through the screen to be collected in the pipe annulus and are flushed from the vessel through a pipe connected to valve C. The screen is sized to retain the filter media, which returns to the vessel. Circulation and backwashing of media lasts 10–20 min. Upon completion of the backwash, the medium is allowed to settle, and the filter returns to normal filtration mode.

6. Conclusions

This review summarizes currently investigated and applicable oil sorption media including both natural and synthetic media. The main focus is on polymeric foams and smart carbon foams (carbon nanotube- and graphene-based aerogels), which may be suitable candidates for the replacement of traditional media such as walnut or pecan granules in the future. The review also comprises the inventions for oil/water separation technologies through deep-bed filtration including filtration media, technological configurations, and regenerating procedures as well as the current laboratory setups for testing oil/water deep-bed filtration.

As a summary of this review, it can be concluded that the effectiveness of separating emulsified oil through deep-bed filtration using traditional media mainly depends on the ability of these media to adsorb oil in a sufficient amount and promote coalescence of oil droplets; the latter seems to be the key separation mechanism. The walnut shell granules are almost solely used in the water treatment industry due to their good performance imparted by their well-balanced surface polarity (surface free energy), roughness, good mechanical properties protecting them against abrasion, wide availability and low price. Simple oil removal from the surface makes them superior over other similar materials. On the other hand, the potential of polymeric materials has not yet been fully exploited, which may be an alternative to the current media. The potential of these materials is based on their broad availability and low price (particularly for polyolefins), simple treatment of their surfaces through a variety of chemical and physical methods to design surfaces with tailored surface free energy (wettability), and porosity. Moreover, all these materials can be obtained from recycled polymers, particularly polyethylenes of various grades, which otherwise have little recycling potential. The advantage of polymers especially excels when foamy adsorption media has been considered. The very recent research tends in this direction. Various kinds of carbon-based foams and sponges have been investigated and are reviewed in this paper. The sponges have a great ability to absorb a high amount of oil within their internal structure, which often comprises over 90 vol.% of free pores. This feature of foams is generally employed for the remediation of oil spills. However, the adsorption of free oil significantly differs from the adsorption of oil from emulsions. In the latter process, for example, in the case of frequently employed sponges, such as polyurethane melamine-based sponges (common kitchen sponges), an emulsion usually penetrates into the sponge bulk without any observable separation of components.

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