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Review

Recent Advances in Functional Materials for Wastewater Treatment: From Materials to Technological Innovations

Nadia Khan [1], Zahra A. Tabasi [2,*], Jiabin Liu [2], Baiyu H. Zhang [2] and Yuming Zhao [3,*]

1 Faculty of Science, Memorial University of Newfoundland, St. John's, NL A1B 3X5, Canada; nadiak@mun.ca
2 Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, NL A1B 3X5, Canada; jiabin.liu@mun.ca (J.L.); bzhang@mun.ca (B.H.Z.)
3 Department of Chemistry, Memorial University, St. John's, NL A1B 3X7, Canada
* Correspondence: zat077@mun.ca (Z.A.T.); yuming@mun.ca (Y.Z.)

Abstract: The growing concerns about climate changes and environmental pollution have galvanized considerable research efforts in recent years to develop effective and innovative remediation technologies for contaminated soils and water caused by industrial and domestic activities. In this context, the establishment of effective treatment methods for wastewater has been critically important and urgent, since water pollution can take place on a very large scale (e.g., oceanic oil spills) and have massive impacts on ecosystems and human lives. Functional materials play a central role in the advancement of these technologies due to their highly tunable properties and functions. This article focuses on reviewing the recent progress in the application of various functional materials for wastewater treatment. Our literature survey is first concentrated on new modification methods and outcomes for a range of functional materials which have been actively investigated in recent years, including biofilm carriers, sand filters, biomass, biopolymers, and functional inorganic materials. Apart from the development of modified functional materials, our literature survey also covers the technological applications of superhydrophilic/superhydrophobic meshes, hybrid membranes, and reusable sponges in oil–water separation. These devices have gained significantly enhanced performance by using new functional materials as the key components (e.g., coating materials), and are therefore highly useful for treatment of oily wastewater, such as contaminated water collected from an oil spill site or oil–water emulsions resulting from industrial pollution. Based on our state-of-the-art literature review, future directions in the development and application of functional materials for wastewater treatment are suggested.

Keywords: wastewater treatment; functional materials; surface modifications; adsorbents; superhydrophilic; superhydrophobic; membrane; mesh; sponge; nanomaterials; oil–water separation; oil spill management

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1. Introduction

Wastewater is predominately discharged from domestic, industrial, and public facilities. Wastewater may contain a variety of inorganic and organic pollutants, as well as microorganisms, depending on its source(s). For example, modern manufacturing and processing industries continuously release heavy metal ions, textile dyes, and other toxic chemicals to contaminate ground water and surface water. In offshore oil and gas industrial activities, oily wastewater is massively produced during oil and gas exploration, processing, treatment, and accidental oil spills. The increasing environmental impacts by wastewater in recent years have raised growing concerns globally. If not treated timely and properly, the accumulated wastewater can lead to irreversible damages to natural ecosystems and impose serious risks to human health.

Specially designed functional materials have played an important role in combating environmental pollution. Over the past few years, the technologies of wastewater treatment have been greatly advanced by the application of various functional materials. Many novel functional materials are derived from modifications of conventional organic and inorganic materials as well as sustainable biomass and natural polymers. On the other hand, nanotechnological products such as functional nanoparticles, carbon nanofibers/nanotubes, and nanoporous materials have emerged as high-performance modifiers to dramatically change the surface properties of adsorbent materials and separation devices (e.g., meshes, membranes). With these materials, pollutants in wastewater can be effectively removed from the adsorption or phase separation approach even under harsh conditions. In this article, we provide a review of recent studies and technological breakthroughs made in the development and application of functional materials for wastewater treatment. Our discussions are specifically focused on modified functional materials and material-based technologies. At the end of this paper, new research directions and opportunities are forecast based on our literature survey.

2. Application of Functional Materials in Wastewater Treatment

Functional materials for wastewater treatment can be fabricated based on naturally existing or synthetic sources [1]. Herein our discussions of the recent studies in this area are made according to the functionality and chemical nature of the materials used.

2.1. Biofilm Carriers

Biofilms are one of the most commonly used materials in wastewater treatment. It acts as a biological filler in an aerated tank and wetland for the growth and adhesion of microorganisms. The biofilm itself does not effectively remove pollutants; however, it shows good resistance to the degradation caused by microorganisms, owing to its rough and durable surface. Biofilm carriers are mainly elastic fillers made from polymers or ceramsite materials such as shale, volcanic rock, and clay. Ceramsite is the most widely used biofilm carrier for wastewater treatment [1]. The shape and strength of ceramsite particles depend on manufacturing processes. In recent years, a variety of raw materials such as fly-ash, river sludge, steel slag, straw, and sewage sludge have been used as biofilm carriers. Compared with the traditional ceramsites, these new materials show better performance in biofilm growth and removal of nitrogen, phosphorous, organic matter, and heavy metals.

In 2021, Amshawee et al. [2] contributed a systematic review on the importance of biofilm carrier roughness in facilitating the growth of microorganisms by providing substratum for their attachment. It has been concluded that increased roughness enhances surface wettability to protect the microbial communities from being detached. Wang and co-workers [3] used different types of biofilm carriers, such as carbon fibers, polyurethane, or non-woven fabrics, to fabricate a fixed-bed baffled reactor for removal of nitrogen from synthetic aquaculture wastewater by means of microbial nitrification and denitrification reactions. Their work showed that carbon fibers have a great potential in aquaculture wastewater treatment, and different types of biofilm carrier materials influence the biofilm formation in different ways. Makisha et al. [4] studied five types of polymer biofilm carriers in order to achieve improvement on secondary wastewater treatment for removing organics and nutrients in an aerobic reactor. They investigated the performance of three benches filled with a floating carrier with a filling percent of 10%, 20%, and 30%, respectively. Their study showed 95–96% effective BOD (biochemical oxygen demand) removal in filling ratio benches and 92% removal in a control bench that contains no floating carriers. For ammonia nitrogen, the removal efficiency of the control bench was only 55%, while floating carriers helped to increase the efficiency up to 70–86%. The above-mentioned studies on biofilm carriers in recent years are summarized and compared in Table 1.

Table 1. Recent studies of biofilm carriers for removal of organics and nutrients in secondary treatment.

Authors (Year)	Materials Used	Outcomes
Amshawee et al. (2021)	Biofilm carrier	Roughness enhances wettability and protects microbial communities from detachment.
Wang et al. (2021)	Carbon fibers, polyurethane, non-woven fabrics	Carbon fibers show more potential in aquaculture wastewater treatment.
Makisha et al. (2021)	Polymer biofilm carriers	The removal efficiency is enhanced by increasing the ratio of the floating carrier.

2.2. Sand Filters

Sand has been for a long time used as a filter for the treatment of wastewater, drinking water, and other water purification processes. Sand is a simple and low-cost material, but lacks the capability of removing toxic and harmful substances. Currently, active research is being conducted on how to improve the performance of sand filters in terms of surface, mechanical, and adsorption properties. In 2018, Chen et al. [1] investigated quartz sand as a functional carrier. With a method of repeated heating and steaming, they prepared a type of aluminum salt-modified quartz sand, which gave an excellent performance in algae removal in comparison with unmodified quartz sand filter. Saini and co-workers [5] in 2021 designed a simple and cost-effective method for the treatment of wastewater generated by household, canteen and the laboratory of an academic institute. The study explored the removal of metal ions and phosphate ions from wastewater by using plant species, such as Typha latifolia L. and Canna indica, through the phytoremediation process. The various water quality parameters were analyzed. Their method achieved a significant reduction in hardness, turbidity, and chemical oxygen demand, as well as an increase in dissolved oxygen value. The treated water could be brought into various uses such as household works and agriculture. Very recently, Yan et al. [6] investigated the performance of superhydrophilic and superhydrophobic quartz sand filters with Janus channels in the separation of surfactant stabilized oil-in-water and water-in-oil emulsions. Based on computational and experimental studies, they concluded that the Janus channels in the mixed sand layer give better demulsification capability and separation performance, due to high interaction energy with emulsified oil droplets. The as-prepared Janus sand filter showed excellent recyclability, environmental friendliness and great potential in the separation of surfactant stabilized oil–water emulsions. Table 2 compares the two recent studies on modified sand filters as mentioned above.

Table 2. Recent studies of sand filters for demulsification and separation oil/water mixtures.

Authors (Year)	Materials Used	Outcomes
Saini et al. (2021)	Typha latifolia L. and Canna indica	Significant reduction in hardness, turbidity and chemical oxygen demand. Dissolved oxygen value are increased.
Yan et al. (2021)	Quartz sand filter with Janus channels	The Janus channels exhibit excellent demulsification capability and separation performance.

2.3. Biomass Materials

Rice-husk (RH), coconut shells, and sawdust are excellent sources of biomass materials. RH is an agricultural by-product that can be used for the removal of cationic dyes (e.g., methylene blue) and crystal violet (methyl violet) from wastewater. Compared with other adsorbents, RH shows low adsorption capacity for various dyes, but its low costs and abundant availability are advantageous for large-scale industrial application; for example, removal of dyes from textile wastewater [7]. Another important application of this type of materials can be found in the production of biochar using palm kernel shell as an efficient and cost-effective adsorbent to remove dyes from wastewater [8]. An intriguing honeycomb like carbon foam was recently produced by Tan et al. [9] from larch sawdust and this material can serve as a hydrophobic adsorbent for oil spill cleanup. To make such adsorbent, liquefied-larch based polymer foam (LLB-PF) and its carbonized products were prepared. It has been found that 3D interconnected and open cell honeycomb structures still remain intact even after the carbonization process. These two ultra-light foams exhibited rapid adsorption capacity not only for oils but also for organic solvents. A comparison of these two studies of biomass materials is made in Table 3. It is worth noting that a comprehensive review was published by Vishnu and co-workers in 2022 [10], summarizing the application of different types of adsorbents produced from agricultural waste, activated carbons, nanomaterials, and biomaterials.

Table 3. Recent studies of biomass for removal of oils and dyes from wastewater.

Authors (Year)	Materials Used	Outcomes
Tan et al. (2018)	liquefied-larch based polymer foam	This ultra light foam exhibits rapid adsorption capacity for oils and organic solvents.
Quansha et al. (2015)	Agricultural by-products (e.g., peanut husk, wheat straw)	Dyes can be removed by these materials.

2.4. Chitosan-Based Biopolymers

Chitosan is a mucopolysaccharide found in the shell of crabs and shrimps (Figure 1), usually obtained by treating the shell with sodium hydroxide. In this reaction, the acetyl groups of the biopolymer are hydrolyzed, leading to the formation of free primary amino groups in the molecular structure of the biopolymer. Chitosan has been recognized as an alternative adsorbent for the removal of copper, chromium, and dyes from wastewater.

Figure 1. Chitosan from marine crustacean products (picture adopted from https://zenonco.io/cancer/chitosan/ accessed on 2 February 2022).

Due to the presence of free primary amino sites, the adsorption of dyes and formation of chelates with metal ions under acidic conditions can occur easily, making chitosan a suitable and cost-effective option for the adsorptive removal of various pollutants from wastewater. Chitosan is readily soluble in water, even in weakly acidic aqueous solutions. Many research works on chitosan in the past few years were focused on developing methods for reducing its solubility. Cross-linking the chitosan chains through reacting their amino sites with cross-linking agents is an effective approach for making low-solubility chitosan. On the other hand, cross-linking reduces the adsorption capability of chitosan. Using carbon tetrachloride as a cross-linking agent, Ramnani and Sabharwal [11] reported a radiation-assisted method, in which chitosan was cross-linked in a ^{60}Co gamma irradiation chamber. Through this treatment, the cross-linked chitosan attained a much better adsorption capacity than chemically cross-linked chitosan. Li et al. [12] in 2015 investigated a method of coating silica gel particles on chitosan. The resulting materials showed high surface areas which allow easy access to active amino sites. The modification methods and adsorptive performance of the chitosan materials in the above-mentioned studies are summarized and compared in Table 4. The readers are also referred to a very recent review authored by Upadhyay et al. in 2021, which has comprehensively summarized the performance of chitosan-based adsorbents for removal of heavy metal ions [13]. Moreover, that review article has discussed the common chitosan modification methods and the design of chitosan-based adsorbents in fixed bed column packaging for industrial wastewater treatment. It has been concluded that cross-linking and grafting are the most popular methods. Chitosan-based adsorbents in column bed packaging perform much better than commercial adsorbents in the continuous flow process.

Table 4. Studies on chitosan-based functional materials for adsorptive application.

Authors (Year)	Materials Used	Outcomes
Ramnani et al. (2006)	Carbon tetrachloride-crosslinked chitosan	Improved adsorption capacity, and less soluble in acid.
Li et al. (2015)	Silica gel particle-coated chitosan	Surface area and adsorption capacity are increased.

2.5. Inorganic Materials

Functional materials based on carbon or minerals belong to the category of inorganic functional materials. Recent studies on their applications in wastewater treatment are discussed below.

2.5.1. Carbon Adsorbents

Carbon adsorbents have wide applications in the removal of color, odors, organic matters, dyes, organic pollutants, disinfection by-products, insecticides, free chlorine, and heavy metals from wastewater [1]. Physical and chemical activation processes are commonly used to prepare activated carbon as adsorbent materials. Activated carbon is amorphous in structure and displays a large specific surface area that is beneficial for adsorption (Figure 2).

Figure 2. Morphology of activated carbon.

Physical activation is usually done through high-temperature carbonization (500–900 °C) of gases such as carbon dioxide (CO_2) and nitrogen (N_2). Chemical activation process involves oxidative treatment of carbon with an oxidizing agent, such as zinc chloride ($ZnCl_2$), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), and nitric acid (HNO_3), to create more active sites and increase adsorption capacity. The production of some types of activated carbon involves high-energy consumption and the use of expensive chemicals or raw materials. These conditions make them less economical. In order to reduce the production cost, agricultural and industrial wastes have been investigated as the raw materials for activated carbon. Tabbakh et al. in 2018 [14] prepared activated carbon from three different types of agricultural wastes (wheat straw, uncooked and cooked corn cob) through the chemical activation method. Their study showed that cooked corn cob gives excellent adsorptive performance in removing oil. Rashidi et al. in 2017 reported the production of palm oil-based activated carbon through a microwave processing method [15]. This activated carbon shows an excellent potential in removing dyes from wastewater. In 2020 Oboh et al. [16] used coconut coir to prepare activated carbon. Their studies indicated that treatment with a chemical activation reagent, KOH, could lead to activated carbon useful for adsorption of spilled crude oil in water. Marques et al. [17] studied the effects of time on steam activation. According to the results obtained from three different activation times, a long activation time is necessary for achieving a larger BET (Brunauer–Emmett–Teller) surface area. This can be reasoned by that the carbon material needs a sufficiently long time to react with an activating agent. Monsalvo et al. [18] investigated the effects of temperature and reaction time on the production of sewage-based activated carbon through carbon dioxide activation. Their results showed that increasing activation time can significantly improve the surface area from 20 m^2/g to 94 m^2/g at 800 °C. Mohamed et al. [19] optimized the activation conditions for activated carbon in order to improve surface area and micropore volume. The highest surface area and micropore volume were achieved at 838 °C and 80 min contact time.

Although activated carbon produced from agricultural and industrial wastes is economical and applicable in environmental protection, its adsorption capacity is not very high in comparison to other types of active carbon such as those prepared from coconut shell and coal. In order to overcome this limitation, Malik et al. [20] modified activated carbon with nitric acid to make it selective towards lead, while the same material modified by air oxidation is selective towards copper. Shim et al. [21] modified activated carbon fibers with nitric acid and sodium hydroxide. They found that the acid-modified carbon achieved a significant improvement in removing copper and nickel from an aqueous solution.

Sun et al. [22] in 2013 prepared superhydrophobic activated carbon sponges by coating highly porous activated carbon onto a sponge skeleton using a simple dip-coating method followed by polydimethylsiloxane (PDMS) treatment. They applied such treated sponge in treatment of a wide range of organic matters and oils, and the results showed excellent absorption selectivity and efficiency. On the basis of their results, it was concluded that the treated sponge has a great potential in removal of organic contaminants or oil from water. Furthermore, the study suggested a new approach for the development of carbon adsorbents with high absorption efficiency and selectivity for oil spill cleanup and wastewater treatment. Deng et al. [23] in 2021 modified the coconut shell-based activated carbon with different activating agents, including acid, alkali, potassium permanganate, and iron salts. The removal efficiencies for heavy metals (Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+}) were determined. It was found that 1 g dosage of the adsorbent modified by the above agents could remove more than 90% of pollutants from wastewater. In 2021 Nizam et al. [24] used biomass–based powdered activated carbon (PAC) to remove anionic and cationic dyes from an aqueous solution. The PAC was made through carbonization and activation with the aid of KOH, NaOH, and H_2SO_4. The results of this study showed that various functional groups (hydroxy, alkoxy, carboxyl, and π-units) are present at the active sites, which facilitate the adsorption of dyes from industrial wastewater. Table 5 summarizes the types and performance of activated carbons for wastewater treatment in the above-mentioned studies.

Table 5. Recent studies on modified activated carbons for watstewater treatment.

Authors (Year)	Carbon Sources	Outcomes
Tabakah et al. (2018)	Agricultural waste	Excellent adsorption capacity for oil is attained by cooked corn as the carbon source.
Rashidi et al. (2017)	Palm oil	Excellent potential for dye removal.
Monsalvo et al. (2011)	Sewage	Improve surface area through control of activation time temperature.
Deng et al. (2021)	coconut shells	Effective removal of pollutants and heavy metals in wastewater.
Nizam et al. (2021)	biomass-based powdered activated carbon	Functional groups and active sites are responsible for adsorption and removal of dyes from wastewater.

2.5.2. Zeolite

Zeolite is a microporous material containing hydrated aluminosilicate of sodium, potassium, and calcium ions with good cation exchangeability (Figure 3).

Figure 3. Photography of a zeolite.

Zeolite can be used as a cation exchanger for reducing the hardness of water. Zeolite possesses advantageous morphological and structural properties, such as unique pore characteristics, excellent chemical, thermal and mechanical stability, low energy consumption, and anti-biofouling surfaces. Zeolite has been widely used in purification of oil, cleanup of petroleum contaminated sites and industrial wastewater. The adsorption mechanism depends on the textural properties such as the ratio of mesopores in the zeolite structure and the physicochemical properties of the organic pollutant. For example, Panayotova [25] treated a natural zeolite ore with sodium hydroxide (NaOH), sodium chloride (NaCl), and sodium acetate (CH_3COONa) to produce a synthetic zeolite with improved ion exchange capacity. The major drawback of zeolite is its low permeability. In turbid water, the colloidal particles present can easily clog the pores of zeolite to decrease the flux rate and permeability. In order to overcome this problem, composite zeolite is used. Composite zeolite is the combination of synthetic zeolite and diatomite. The presence of diatomite affords macropores that enable the composite to retain a high flow rate. Iucolano et al. [26] in 2005 used a zeolite tuff to remove barium ion (Ba^{2+}) from wastewater. It was first mixed with Portland cement and water. Then the mixture was cured for 28 days. Their study showed that the efficiency of tuff in removing barium ion can be improved by increasing the amount of cement in the production.

In 2021, a comprehensive review was reported by Rad et al. [27], covering the recent studies on the capability of zeolite based composites in the forms of zeolite/inorganic and zeolite/polymer for the adsorption of toxic matters such as heavy metal ions, dyes, herbicides, and drugs from water. It has been concluded that a number of adsorption mechanisms (surface adsorption, chelation, ion exchange, electrostatic interaction, diffusion, and complexation) are responsible for the adsorption of different toxic matters. The capability of zeolite-based composites for the removal of toxic matters from water was compared with that of raw zeolite. The results pointed to a great potential of the zeolite-based composites in wastewater treatment. Abdelrahman et al. [28] in 2021 synthesized a group of low-cost nanosized zeolite, zeolite/zeolite, and geopolymer/zeolite products by using rice husk as the silicon source and waste aluminum cans as the aluminum source. These materials were found useful for removing Co(II), Cu(II), and Zn (II) from aqueous media and wastewater, showing spontaneous uptake of metal ions and Langmuir-type adsorption isotherms. The above studies on synthetic zeolites and their application in removal of toxic ions from wastewater are compared and summarized in Table 6.

Table 6. Recent studies on synthetic zeolites for ion removal.

Authors (Year)	Materials Used	Outcomes
Panayotova et al. (2001)	Natural zeolite ore, NaOH, NaCl, CH_3COONa	The synthetic zeolite exhibits better ion exchange capacity.
Iucolano et al. (2005)	Zeolite tuff, Portland cement, water	Removal efficiency for Barium increases with increasing Portland cement concentration.
Rad et al. (2021)	Zeolite/inorganic, zeolite/polymer	Great potential in removal of toxic matters.
Abdelrahman et al. (2021)	Rice husk and aluminum cans	Uptake of metal ions follows a Langmuir isotherm.

2.5.3. Silica Aerogels

Silica aerogels are nanoporous silicon oxide solids (Figure 4), which are made by extracting liquid from the framework of silica in a way that they preserve most of the orignal framework volume. As such, silica aerogels take an open foam-type structure, featuring very large surface area, high porosity, low thermal conductivity, and low density. The unique morphological and interfacial properties make silica aerogels excellent adsorbents for various applications.

Figure 4. Photography of silica-based aerogels.

Hrubesh et al. [29] in 2001 modified silica aerogels with perfluoro functional groups such as CF_3 (trifluoromethyl) for adsorption of various organic solvents. Their results showed that the CF_3-modified silica aerogels gain higher adsorption capacity for solvents than granular activated carbon (GAC). Reynolds et al. [29] compared the performances of CF_3-modified aerogels with other absorbent materials previously developed. Their results indicated that CF_3-modified aerogels in the non-powder form give better absorption capacity than in the powder form. They also suggested that CF_3-modified aerogels could be applied as coating on devices to achieve better adsorbent performance. Selective adsorption of oil in the presence of water was achieved, suggesting an application in oil spill recovery. Wang et al. [30] in 2012 examined the effectiveness of purchased Cabot nano-gel 301 and 302 at removal of different types of oils, such as vegetable, motor and crude oils. The oil uptake values were found in the range of 11.7–15.1 g (oil)/gram (aerogel). The large scale production of hydrophobic silica aerogels is very cumbersome and expensive, because of complicated drying techniques involved and the high costs of silica precursors. In order to overcome this barrier, Sorour et al. [31] in 2016 developed an economical method for preparing hydrophobic silica aerogels and investigated their application in oil spill cleanup. The synthetic process involved an ambient pressure drying technique, using inexpensive aqueous sodium silicate solution and hexamethyldisilazane (HMDS) silica as precursors. This synthetic method allows hydrophobic silica aerogels to be prepared in an easy, low-cost, and time-saving manner. For example, the unit cost of its production is in the range of $1.20–2.84/kg. The produced hydrophobic silica aerogels show large surface area, low density, and high porosity. All of these attributes enable them to show excellent sorption performance in treating oily wastewater that contains dispersed oils or emulsified oils. It is worth noting that removal efficiency up to 96% was achieved by applying these silica aerogels in saline and non-saline oily wastewater. Gopi et al. [32] in 2017 developed a hybrid bioaerogel as a multifunctional material for wastewater treatment. They used cellulose that contains both crystalline and amorphous structures and converted it into cellulose nanofibrils. Another biomaterial called chitin was also used in their work. Chitin can be extracted from shrimp and developed into chitin nanocrystals by removing the amorphous components. A hybrid bioaerogel was made by decorating chitin nanocrystals on a 3D cellulose aerogel. Herein, chitin nanocrystals were applied as reinforcing nanoparticles to compensate the low mechanical strength and chargeless surface of cellulose nanofibrils. By this way, the hybrid materials achieved very high adsorption capacity in removal of methylene blue and rhodamine dyes from wastewater. Recent progress in the development of functional silica aerogel materials for wastewater treatment is summarized in Table 7.

Table 7. Recent studies on modified silica aerogel for adsorptive applications.

Authors (Year)	Materials Used	Outcomes
Hrubesh et al. (2001)	Perfluoro carbon	The modified silica aerogel shows better adsorption capacity than granular activated carbon.
Reynold et al. (2001)	Other absorbing materials	The modified silica aerogel is a non-powder form and exhibits high adsorption capacity.
Wang et al. (2012)	Cabot nanogel 301, 302	Effective removal of vegetable, motor and crude oils from water. The method is relatively expensive.
Sorour et al. (2016)	Sodium silicate and hexamethyldisilazane silica	Efficient and economic cleanup of oil spill.
Gopi et al. (2017)	Chitin nanocrystals coated on 3D cellulose aerogel	Excellent adsorption capacity for removal of methylene blue and Rhodamine dyes.

2.5.4. Fly-Ash

Fly-ash is a combustive residue produced by power industries. Fly-ash is an extremely fine powder rich in silica, alumina, and iron oxides (Figure 5). It has been commonly used for the removal of heavy metals and organic compounds from an aqueous solution.

Figure 5. Photography of fly-ash.

Gupta and Ali [33] in 2004 studied bagasse fly-ash for removal of heavy metal ions such as lead, chromium, cadmium, nickel, copper, and zinc. In 2007, Cao et al. [34] prepared fly-ash modified with polydimethyldiallylammonium chloride (PDMDAAC), which showed a four-time increase in adsorption of anionic dyes in comparison with unmodified fly-ash. The significantly improved adsorption performance can be attributed to the incorporation of PDMDAAC which changes the surface charge of fly-ash. Wang et al. [35] reported a method of treating fly-ash with nitric acid for 24 h at room temperature. This modification led to increased surface area and pore volume. As a result, the modified fly-ash gained an adsorption capacity for methylene dyes three times greater than that of untreated fly-ash. Most recently, Gadore et al. [36] studied the performance of modified fly-ash in removal of various pollutants such as phenols, dyes, heavy metal ions, pesticides, and many other organic and inorganic ions like fluoride and phosphates in wastewater. This study extended the application of modified fly-ash to the field of water remediation. A summary of the recent studies on modified fly-ash in adsorptive application is provided in Table 8.

Table 8. Recent studies on modified fly-ash materials for adsorptive application.

Authors (Year)	Materials Used	Outcomes
Gupta et al. (2004)	Bagasse fly-ash	Effective removal of cadmium, chromium, nickel and other heavy metals.
Cao et al. (2007)	Treated fly-ash with poly(dimethyldiallyl) ammonium chloride	Four-fold enhancement in adsorption of anionic dyes.
Wang et al. (2005)	Fly-ash treated with nitric acid	Adsorption capacity for methylene dye is three times higher than the untreated fly-ash.
Gadore et al. (2021)	Fly-ash	Effective water remediation.

2.5.5. Clay Minerals

Clay minerals are hydrous aluminium phyllosilicates with variable amounts of metal cations such as iron, magnesium, alkali and alkaline metals (Figure 6). Clay minerals contain small crystalline particles with anionic surface due to the presence of silicates. Positively charged cations, such as aluminum, magnesium, sodium, potassium, and calcium, known as exchangeable cations, can be attracted toward the surface of clay minerals through electrostatic interactions.

Figure 6. Photography of clay minerals.

The surface of clay minerals is hydrophilic, which facilitates the formation of a water layer on it. Clay minerals can adsorb inorganic cations more readily than hydrophobic organic constituents from water. Recently, the need for the development of organophilic clay has increased in order to utilize clay as an adsorbent for removal of organic pollutants from wastewater. Organophilic clay can still retain the advantageous properties of clay, such as high inherent porosity and surface area. On the other hand, its affinity for organic species, such as diesel, jet fuel, and kerosene, is significantly improved compared with typical clay minerals. For this reason, organophilic clay has captured great attention as a candidate material for oil spill cleanup. Moazed and Viraraghavan [37] explored the potential of powdered bentonite organoclay in removal of oil from oil-in-water emulsion. Alther [38] demonstrated that granular organoclay is more effective than activated carbon in removing a wide variety of oily residues from water. It is worth mentioning that the clogging problems that plague the application of activated carbon are much less significant in granular organoclay, adding another beneficial feature for its real application. Kumari et al. [39] in 2021 conducted a study on the properties of clay minerals and disclose their potential application in many fields. Their studies showed that clay minerals are the main ingredients of the raw material formed in the presence of water. Different structures exist in clay, depends on their mining sources. Small size and distinctive crystal structures of clay can lead to unique properties such as high cation exchange capacity, swelling behavior, specific surface area, and adsorption capacity. Ma et al. [40] in 2022 developed clay-based nanocomposite hydrogels with interesting microstructures. The hydrogel networks showed high mechanical properties and abundant ozone adsorption sites, resulting in an intriguing performance of sustained release of ozone for antibacterial application. A summary of the recent progress in the studies of modified clay minerals is given in Table 9.

Table 9. Recent studies of clay minerals for removal of oil from wastewater.

Authors (Year)	Materials Used	Outcomes
Moazed, Viraraghavan (2002)	Powdered organoclay	Effective removal of oil.
Alther (1995)	Granular organoclay and activated carbon	The granular organoclay is more effective than activated carbon for oil removal.
Kumari et al. (2021)	Clay minerals	High capacity for cation exchange and adsorption.
Ma et al. (2022)	Clay-based nanocomposite hydrogels	Long-term antibacterial effects through ozone adsorption sites.

3. Application of Functional Materials in Superhydrophilic and Superhydrophobic Meshes

3.1. Superhydrophilic Meshes for Oil-Water Separation

Over the past few years, the development of superhydrophilic meshes has attracted increasing attention, owing to their appealing application in separating oil from water. Superhydrophilic meshes show water permeation and oil repelling behavior as schematically illustrated in Figure 7. Water can quickly pass through a superhydrophilic mesh, but oil is repelled and prohibited from passing through it. In this way, oil and water can be quickly separated without causing significant blockage of the mesh pores. Functional materials especially metal oxides such as silicon dioxide, titanium dioxide, and zinc oxide nanoparticles, can induce the formation of micro-hierarchical structures and a large number of pores on the mesh surface, making it exhibit superhydrophilicity. Superhydrophilic surfaces have broad applications, including antifogging screens, windows, lenses, antifouling coatings, and foils for food packaging.

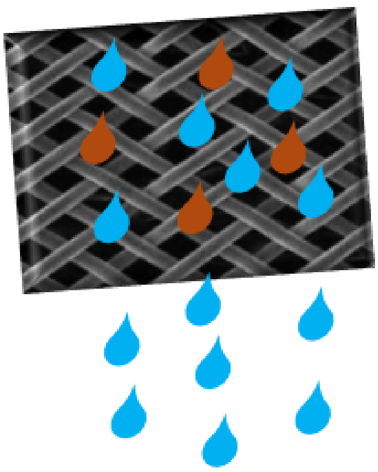

Figure 7. Superhydrophilic mesh for oil–water separation.

In 2012, Yang [41] developed a superhydrophilic and superoleophobic nanocomposite mesh. Modified with silicon dioxide (SiO_2) nanoparticles, the mesh surface attained increased roughness. Another polymer-based coating material, PDDA-PFO (polydially diammonium perfluoroctonate), was also used to attach hydrophilic and oleophobic groups to the mesh surface. In this way, the surface achieved a water contact angle (WCA) of 0° and oil contact angle (OCA) of 155° for different types of oils. This study demonstrated that SiO_2 has a great potential in the treatment of various types of oils, and the efficiency for removal of oil could be enhanced by varying the concentration of SiO_2. The modified meshes became highly efficient in oil removal when the concentration of silica is above 50 wt%. Zhang et al. [42] in 2013 developed a self-cleaning superhydrophilic and underwater superoleophobic mesh. The mesh was prepared by the layer-by-layer assembly of sodium silicate, and titanium dioxide (TiO_2) nanoparticles on a PDDA modified stainless steel mesh. UV-light illumination of the TiO_2 component can be used as a way of self-cleaning, through which the contaminants accumulated on the mesh are photocatalytically decomposed. The particles of sodium silicate and titanium dioxide on the surface of the mesh can be preserved to give excellent wetting properties. The results of the study showed that the prepared mesh could effectively separate water from oil–water mixtures, while good re-usability was attained through UV-illumination for self-cleaning.

Li et al. [12] in 2015 developed a zinc oxide (ZnO)-coated mesh with superhydrophilic and underwater superoleophobic performance. They modified a stainless steel mesh by spraying a mixture of ZnO nanoparticles and waterborne polyurethane (PU) on the mesh surface. This spray coating method is now commercialized and used in large-scale application. The high water affinity and strong underwater oil repellence exhibited by this type of mesh make it particularly effective in gravity-driven oil–water separation. Experimental results showed a water/oil separation efficiency as high as 99%. More significantly, the coated mesh maintains a high separation efficiency and recyclability. After 50 cycles of separation, the separation efficiency for the kerosene-water mixture is still above 97.3%.

A self-cleaning nanoscale carbon hybrid system was developed by Shervani et al. in 2019 [43]. In this work, a steel mesh was coated by layers of polymer-based porous materials and graphene oxide (GO). With this nano-coated mesh, a two-state process was developed to selectively remove hydrocarbons from emulsified water. Reduction in TPHs (total petroleum hydrocarbons) from 290 ppm to less than 1 ppm and more than 99.5% separation efficiency (oil removal from oil–water mixture) have been achieved. It is also worth remarking that no PAHs (polycyclic aromatic hydrocarbons) were detected in the treated water, and the mesh was robust and did not suffer from any fouling problems.

Liu et al. [44] in 2016 developed an effective and simple method for cleaning up oily wastewater. In this research, a superhydrophilic and underwater superoleophobic mesh was developed by spraying chitosan silica nanoparticles–glutaraldehyde composite (CS-SiO_2-GA) on a stainless steel mesh for separation of oil–water mixtures. The developed mesh showed useful properties for oil–water separation, such as biocompatibility, high mechanical, chemical, and thermal strength, good film-forming ability, and hydrophilicity.

Wen et al. [45] in 2013 fabricated a zeolite-coated mesh film (ZCMF) for efficient oil–water separation, which showed excellent superhydrophilic and underwater superoleophobic properties. Due to a gravity-driven mechanism, water could easily pass through the film, whereas oil was retained above the film. Meanwhile, the underwater superoleophobic surface showed a low affinity for oil droplets, thus protecting the film from fouling. Moreover, the films are highly stable under harsh conditions. The results of their study showed that underwater oil contact angle is above 150°, which is an indicative of remarkable underwater superoleophobicity. Because of this, a water cushion can be formed between the oil droplets and the solid surface. The strong repulsive interactions between the water cushion and oil droplets protect the ZCMF surface from fouling by oil during the separation process. Further, the separation efficiency of ZCMF was tested by calculating water flux and intrusion pressure. It was shown that the water flux increases with the increase of the pore size of ZCMF, but the intrusion pressure of oil decreases with increasing pore size of ZCMF.

Agano et al. [46] in 2021 fabricated a superhydrophilic and underwater superoleophobic CuO/TiO_2 mesh for oil–water separation. They used the method of electrochemical anodization for coating CuO nanostructures on the copper mesh. After anodization, the mesh was rinsed with distilled water and air-dried. They deposited TiO_2 on the mesh with a high-rate vacuum coating technique. After deposition, the TiO_2 coated mesh was annealed in an air atmosphere in a tube furnace with a slow temperature ramp-up to 500 °C and maintained at this temperature for 2 h. The annealing step is expected to improve the crystallinity of the TiO_2 film. Needle-like structures were developed on the anodized mesh, which entrapped water between the needles. The rough surface present on the mesh further improved the affinity for water. The hydrophilic nature of TiO_2 allowed water to pass through the mesh. A thin layer of water trapped by the TiO_2 needles further enhanced the surface oleophobicity, thus preventing the oil from passing through the mesh.

Zhang et al. [47] in 2013 developed nanowire-haired inorganic membranes with superhydrophilicity and underwater superoleophobicity. The nanowire-haired membrane was prepared by surface oxidation of a copper mesh in an alkaline aqueous solution with $(NH_4)_2S_2O_8$. The existence of $Cu(OH)_2$ nanowires on the copper mesh greatly enhanced its hydrophilic property. A thin layer of water trapped by the $Cu(OH)_2$ nanowires on the copper mesh would further enhance its surface oleophobicity, thus preventing oil from passing through the mesh. The mesh surface showed a WCA of 0° and an OCA of 155°. These nanowire-haired inorganic membranes show great application potential in separating oil from water.

Xue et al. [48] fabricated a novel superhydrophilic and underwater superoleophobic hydrogel-coated mesh for oil–water separation. The preparation of polyacrylamide (PAM) hydrogel-coated mesh was done by using a photo-initiated polymerization process. After immersing the stainless steel mesh into a monomer solution, UV light was used to start the polymerization process. After polymerization, the mesh was washed to remove excess monomers. Through hydrogel-coating on stainless steel mesh, nanostructured papillae were developed. A water layer was formed at the oil/water/solid interface, which decreased the contact area between oil droplets and the solid surface. This made the oil droplets to easily roll off from the surface. This hydrogel-coated mesh is particularly useful for separating oil from emulsified oil–water mixtures.

Shi et al. [49] in 2016 prepared a three-dimensional (3D) graphene foam for oil–water separation. In this work, a sea shell-based chemical vapor deposition template function technique was used for fabricating the 3D graphene foam, which showed high purity, high porosity, ultralow density, and superbendability. They used a highly abundant shell of oceanic mollusk called scallop, which comprises 95% calcium carbonate ($CaCO_3$) and 5% organic biopolymer. Through a simple calcination process, the biological $CaCO_3$ was converted into calcium oxide (CaO) without destroying its structural framework. After heating the CaO framework, a graphene layer was deposited on the CaO surface, forming a CaO@graphene structure. The oxygen atoms on the CaO template delivered a synergistic effect by absorbing and decomposing hydrocarbons at high temperature and promoting carbon–carbon coupling on the substratum. After chemical etching with dilute HCl and followed by freeze-drying treatment, the 3D graphene foam was generated. The results of the studies showed fast separation efficiency, absorption capacity up to a 250-fold weight gain, and excellent absorption performance towards various oils and organic solvents. This functional material can also be used in other industrial applications such as energy storage and water remediation.

Yu et al. [50] in 2019 prepared a superhydrophilic and underwater superoleophobic stainless steel mesh treated with $Co(NO_3)_2$ and H_2NCONH_2 solutions through a simple hydrothermal process and subsequent calcination. By increasing the reaction time, needle-like Co_3O_4 was densely coated on the mesh surface. The as-prepared Co_3O_4-coated mesh separated various oil/water mixtures with high efficiency (>99.4%) and high flux

(>75,000 $L \cdot m^{-2} \cdot h^{-1}$) even in harsh conditions such as highly acidic, alkaline, and salty solutions. Moreover, the Co_3O_4-coated mesh showed an outstanding antiabrasion performance; after 40 abrasion cycles with sandpaper, it still retained a very good separation efficiency. The excellent anticorrosion and antiabrasion behavior of this Co_3O_4-coated mesh makes it resistant to mechanical damages during oil/water separation. The pristine mesh showed hydrophobicity in air (WCA = 126.86 ± 1.56°) and oleophobicity under water (OCA = 138.45 ± 1.45°), but after coating with Co_3O_4 it showed superhydrophilicity in air (WCA ≈ 0°) with an increase in underwater oleophobicity (OCA = 151.19 ± 0.19°).

Sun et al. [51] in 2020 reported a green and facile method for modification of stainless steel mesh through immersion into an oxidation solution (ammonium persulfate and sodium hydroxide aqueous solution) and a conversion solution (tannic acid with pH of 2.4 adjusted by phosphate acid aqueous solution). In the first step, FeOOH clusters were formed and then converted to a complex with tannic and phosphoric acids to make a film on the surface of mesh. The grafting of tannic and phosphoric acid with plenty of peony-like microspheres in the intervals between the wires of the stainless steel mesh improved the surface energy, superhydrophilicity, and superoleophobicity, which are beneficial for oil–water separation and antifouling performance. Long-term durability and resistance were observed even under harsh corrosion and abrasion conditions with oil rejection above 99%.

Mahmodi and co-workers [52] in 2020 synthesized a NaA-type zeolite-coated mesh by a secondary growth method. The aluminum/silicon ratio (ASR) was controlled by varying the amounts of sodium hydroxide, sodium aluminate, and sodium metasilicate monohydrate in aqueous solutions. ASR of 1.21 led to a mesh showing the highest oil–water separation efficiency with superhydrophilicity (WCA = 0°) and underwater superoleophobicity (OCA = 163.7°). Changing the ASR from 0 to 1.21 caused a decrease in the pore size of the mesh from 150 µm to about 10 µm, as a result of the aggregation of NaA zeolite. In the meantime, the roughness of the surface and the oil rejection rate were increased with increasing ASR, while the water flux rate was reduced. Re-usability of the zeolite mesh was demonstrated by implementing a re-calcination process at 550 °C for 6 h. The ASR decreased slightly in each cycle of re-calcination, which is due to dealumination of the zeolite along with the burning of organic components. The average oil rejection rate remained more than 99.4% after three cycles of re-calcination. The results indicated that the zeolite-coated mesh is applicable for separating oil/water mixtures.

Zhang et al. [53] in 2021 developed a novel superhydrophilic/underwater superoleophobic mesh that gave excellent oil/water separation performance. With the use of an inorganic nanomaterial ($MnCo_2O_4$), microscale cube-like structures were developed on the surface of a stainless steel mesh through a facile hydrothermal-annealing process. The resulting $MnCo_2O_4$-coated stainless steel mesh exhibited good antifouling property, high oil/water separation efficiency, and high flux rate (>63 $L \cdot m^{-2} \cdot s^{-1}$). The nanostructures on the mesh surface gave rise to special wettability, allowing a water layer to form between the mesh surface and oil. This layer acted as a cushion to prevent the oil from directly contacting the mesh surface, resulting in excellent underwater superoleophobic performance. This modified mesh also showed excellent corrosion resistance, recyclability, and long-term durability under harsh environmental conditions, which are advantageous for application in oily wastewater treatment. Table 10 summarizes the recent investigations on functional material-based superhydrophilic meshes and their applications in oil–water separation.

Table 10. Recent studies on meshes coated with superhydrophilic materials for various applications.

Authors (Year)	Materials Used	Outcomes
Zhang et al. (2013)	Sodium silicate, titanium dioxide nanoparticles, PDDA, stainless steel, UV light.	The mesh shows self-cleaning superhydrophilic and underwater superoleophobic performance.
Agano et al. (2021)	Copper oxide nanoparticle, titanium dioxide, copper mesh	The coated titanium oxide needles trap a thin layer of water to enhance surface oleophobicity.

Table 10. *Cont.*

Authors (Year)	Materials Used	Outcomes
Xue et al. (2011)	Acrylamide hydrogel, UV light	The developed nanostructured papillae trap a water layer to enhance oleophobicity.
Shi et al. (2016)	Shell of oceanic mollusk and graphene.	3D graphene foam with absorption capacity up to 250-folds weight gain.
Yu et al. (2019)	$Co(NO_3)_2$ and H_2NCONH_2 solutions	Needle-like Co_3O_3-coated mesh shows superhydrophilicit and /underwater oleophobicity.
Sun et al. (2020)	Ammonium persulfate and sodium hydroxide aqueous solution	The grafting of tannic and phosphoric acid on stainless steel mesh improves the surface energy, superhydrophilicity, and underwater superoleophobicity.
Zhang et al. (2021)	Sodium hydroxide, sodium aluminate, sodium metasilicate monohydrate aqueous solutions	Separation efficiency of oil–water is dependent on the aluminum/silicon ratio (ASR). The mesh shows superhydrophilicity and underwater superoleophobicity.

3.2. Superhydrophobic Meshes for Oil-Water Separation

A superhydrophobic surface shows repellance to water but affinity for hydrophobic oil. When a mesh is coated with a superhydrophobic material, it can give oil–water separation performance as illustrated in Figure 8. Unlike the superhydrophilic meshes discussed above, a superhydrophobic mesh allows oil to penetrate but rejects the passage of water.

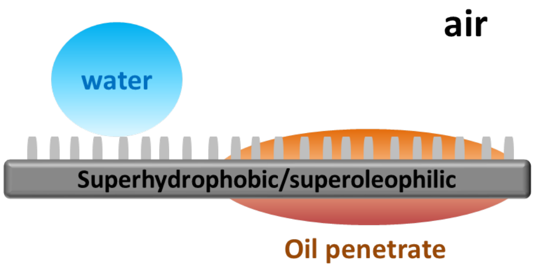

Figure 8. Superhydrophobic mesh for oil–water separation.

Wang et al. [54] in 2015 prepared superhydrophobic and superoleophilic fabrics for separation of oil–water mixtures using polydopamine as an adhesive agent. In this research work, nanoparticles such as silica were immobilized onto the surface of cotton fabrics through mussel adhesive proteins such as polydopamine. Dopamine, through self-polymerization, formed strong covalent and non-covalent interfacial interactions with all types of substances. The strong bioadhesion of PDMS/silica (SiO_2) composite allowed superhydrophobic and superoleophilic coatings to be strongly bound to the surface of the fabrics. The modified fabrics showed superhydrophobicity, low surface energy, and micro/nano-hierarchical structures on their surfaces. A mesh made of these fabrics gave a water contact angle of more than 153 °C. Water droplets could be completely bounced off from the surface of the fabrics without leaving any residual water on it. However, when an oil such as toluene or linseed was applied on the prepared fabrics, the oil would quickly wet the surface by forming a large spreading radius as a result of oleophilicity. The mesh led to oil–water separation efficiency as high as 99% up to 90 cycles of ultrasonic treatment. This bioadhesion method can also be used to prepare superhydrophobic oil containment boom, candle soot-coated nickel foam, SiO_2/polystyrene-coated filter paper.

Wang et al. [55] in 2013 prepared a superhydrophobic copper mesh film, analogous to the performance of butterfly wings, for rapid oil/water separation. In their study, the copper mesh surface was modified by an environmentally-friendly electrochemical deposition method. The electroplating of copper nanoparticles was performed on the as-cleaned copper mesh film and followed by a thiol grafting process to fabricate superhydrophobic surface on the surface of the copper mesh. Such modified surface showed high roughness, low surface energy, and excellent superhydrophobicity.

Salehabadi et al. [56] in 2017 developed superhydrophobic and superoleophilic polyurethane sponges, the surface of which was decorated with nanosilica particles. The effect of nanosilica concentration on the final wetting behavior of the sponges was investigated. They used a simple dipping process for the treatment of sponges with modified and unmodified nanosilica particle suspension. After this treatment, a uniform layer of silica nanoparticles was formed on the surface of the sponge. For the untreated sponge, the WCA value is 120°. Despite this high value, it cannot efficiently separate oil/water mixtures due to a high level of water drop stickiness (sliding angle = 180°). In order to increase superhydrophobicity, different loads of hydrophobic nanosilica were used. By the addition of nanosilica, two simultaneous effects (reduction of surface energy and enhancement of surface roughness) occur. Both effects help increase the WCA value and reduce the sliding angle value. This work showed that nanosilica particles have a great potential in separating different oils and organic solvents from water, and the coating of nanosilica is a simple, efficient, and inexpensive method.

Rasouli and co-workers [57] in 2021 fabricated a superhydrophobic and superoleophilic stainless steel mesh-based membrane, using a facile one-stage dip-coating technique, and investigated the effects of silane alkyl chain size, and the ratio of micro-to-nano particles in the coating solid fraction. Silane compounds with short- and long-alkyl chains were used as surface energy modifiers. Increasing the concentration of nanoparticles to 100% led to a decrease in hydrophobicity, and this effect was found to be more pronounced for the short-chain silane modified surface. Flower-like hierarchical microstructures were obtained using the coating solution of silanes with only nanoparticles. The average pore opening for the mesh was decreased from 76 mm in the bare mesh to 48 mm for the coated mesh. Using this type of mesh, a separation efficiency >99% was achieved for kerosene–water mixtures. The influence of solid composition in the coating with hydrophobic nanoparticles (NPs) and microparticles (MPs) on the wetting characteristics of the mesh was also investigated. Modifications of the surface with long silane chains led to greater hydrophobicity than with short-chain silane.

Yue and co-workers [58] in 2020 fabricated a silicone-modified stainless steel mesh via coating the mesh surface with silicone upon transient heating. The electrothermal effect was employed for heating the water-in-crude oil emulsion, reducing the viscosity of the water-in-crude oil emulsion and thus leading to efficient viscous emulsion separation. The as-prepared silicone-modified stainless steel mesh showed combined superhydrophobic/superoleophilic properties and good re-usability.

Du et al. [59] in 2019 prepared a superhydrophobic stainless steel mesh, the surface of which was coated with hierarchical micro/nanostructures. The coating materials were nontoxic graphite and environmentally friendly titanium dioxide, which were applied on the mesh surface by simple brush-painting method. Polydimethylsiloxane and ethyl cellulose were used as adhesives to have the hydrophobic coating bound to the surface of the mesh. The unique inlay-gated structure on the pores of the mesh resulted in good separation efficiency for various water-in-oil nanoemulsions; an separation efficiency higher than 99.9% was reported with the residual droplets smaller than 8 nm. Furthermore, the wettability of the as-prepared mesh showed good resistance to acids, alkaline, salts, organic solvents, and exposure to UV light. After the mesh was abraded by sandpaper, its separation capability was barely affected, indicating good antiabrasion performance.

Zhang et al. [60] in 2020 reported a superhydrophobic stainless steel mesh coated with fly-ash. In their method, fly-ash was first modified by stearic acid, and then bonded to the surface of a stainless steel mesh with the aid of an epoxy resin solution. The coated mesh exhibited superhydrophobicity with a WCA of 153°. The superhydrophobicity could be ascribed to the formation of a protective barrier against moisture/water on the surface of the stainless steel mesh. Oil/water mixtures such as *n*-hexane/water were successfully separated by this mesh, giving an efficiency of over 97% even after 30 cycles of separation. The simplicity, eco-friendliness, and low cost of this method make it practically useful for preparing large-scale superhydrophobic surfaces. Table 11 summarizes the recent studies of superhydrophobic material-coated meshes for separation applications.

Table 11. Recent studies on meshes coated with superhydrophobic materials for separation applications.

Authors (Year)	Materials Used	Outcomes
Wang et al. (2015)	PDMS/silica composite, fabric, polydopamine	WCA > 153°, 99% separation efficiency.
Wang et al. (2013)	Copper nanoparticle, copper mesh, thiol grafting	Superhydrophobic mesh film.
Salehabadi et al. (2017)	Polyurethane sponge, nanosilica particles	Nanoscale silica particles show great potential in separating different organic solvents and oils.
Rasouli et al. (2021)	Silane compounds with short- and long-alkyl functional chains	The long silane generates a more hydrophobic surface than the short silane.
Yue et al. (2020)	Silicone coated on the stainless steel mesh	Efficient separation of viscous emulsion.
Du et al. (2019)	Graphite, titanium dioxide, polydimethylsiloxane, ethyl cellulose	Forming a very good hydrophobic surface for separating various water-in-oil nanoemulsions with the residual droplets smaller than 8 nm.
Zhang et al. (2022)	Fly-ash, stearic acid, epoxy resin	A protective barrier against moisture/water can be formed on the surface of the stainless steel mesh.

4. Application of Functional Materials in Membrane Technologies for Oil-Water Separation

Apart from adsorbent materials and meshes, the application of membrane technology in oil–water separation has received increasing attention in recent years. Figure 9 illustrates the working principle for separating an oil–water emulsion through a membrane. Membrane separation usually gives much higher efficiency than conventional separation methods, particularly for oil–water emulsions. In the separation, a membrane acts as a semi-permeable layer separating the two phases and regulating the transportation between them. As such, only the water fraction of an oil–water emulsion can flow through the membrane to yield clean water. Functional materials play a dominant role in the development of different types of filtration membranes that are effective at separating various types of oil–water mixtures and emulsions, especially surfactant-stabilized emulsions.

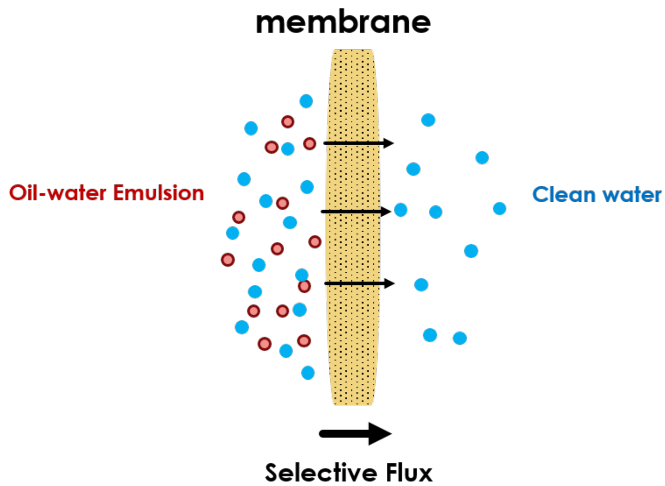

Figure 9. Membrane technology for oil–water separation. The blue circles stand for water droplets and the red circles stand for oil droplets.

The major challenges for the application of membrane technology in oil–water separation are poor flux and rejection rates as well as significant blockage of the membrane pores by oil droplets. Blending membranes with hydrophilic components and coating membrane surfaces with functional materials can be used to improve the membrane separation performance by enhancing the antifouling and hydrophilic properties of modified membranes.

There are three types of filtration membrane technologies for oil–water separation: (1) polymer-based, (2) ceramic-based, and (3) nanomaterial-based. Nanoparticles, especially aluminum oxide (Al_2O_3), titanium dioxide (TiO_2), silicon dioxide (SiO_2), can improve hydrophilicity, permeability, and antifouling properties. Nanoparticles act as both hydrophilic additives and pore-forming agents to improve membrane performance. Furthermore, the flux recovery problems of polymer-based filtration membranes can be addressed through coating with functional nanoparticles. The main drawback of nanoparticles is their poor dispersibility, as they can easily form aggregates, which in turn affect the porosity and permeability of the membrane. To solve this problem, Chen et al. [61] developed a blending method using TEOS (tetraethylorthosilicate), a precursor to SiO_2, to ensure the formation of uniform SiO_2 nanoparticles.

Ceramic-based filtration membranes show high chemical, thermal, and mechanical stability, making them useful for wastewater treatment. However, they are not quite suitable for treatment of oily wastewater, owing to their low permeability, flux rate, and fouling problems. Many studies have been conducted to modify ceramic-based membranes, so that their performance in separating oily wastewater can be significantly improved. A class of nanosized zirconia (ZrO_2)-modified Al_2O_3 microfiltration membranes were prepared by Zhou and co-workers in 2010 [62]. It was found that the nanosized ZrO_2 particles can attract a layer of water molecules through hydrogen bonding, which prevents the membrane surface from contacting oil droplets. As such, the membrane surface gained high hydrophilicity, allowing water to pass through but repelling oil droplets. By this modification, the permeability, flux rate, and antifouling performance of the membrane were improved.

A sol-gel process can be applied, followed by sintering, to generate microcrystals on the surface of ceramic membranes. By this treatment, the surface roughness and area are significantly increased, leading to better separation performance for oily wastewater. On the other hand, the fouling problems are still present after this modification, exerting negative impacts on the separation efficiency. Zhong and co-worker [63] reported a method of using PMMA (polymethylmethacrylate) particles as a hydrophilic component to overcome this problem.

Nanomaterial-based filtration membranes are a type of advanced membranes, which can replace traditional filtration membranes due to the presence of a very thin active separation layer and effective pore sizes. These two important properties improve the performance of the membrane by increasing the flux rate, permeability, and antifouling properties. Nanomaterials such as carbon nanotubes, nanowires, and nanofibers have been applied in making high-performance membranes suitable for the separation of emulsified oil–water mixtures. Recently single-walled carbon nanotube (SWCNT) films have been developed to show ultrafast separation of emulsified oil–water mixtures, with a flux rate 2–3 orders of magnitude higher than that of commercial filtration membranes [64]. Long and co-worker [65] applied MnO_2 nanowires to prepare nanofibrous membranes. The surfaces of these membranes are abundant with oxygen atoms, which can attract water molecules through hydrogen bonding. As such, this type of membranes attained high hydrophilicity. Water could pass through the membrane easily, but oil droplets rolled off from the surface due to high oil rejection rates. As an alternative to this strategy, $Cu(OH)_2$ nanowire-haired copper mesh membranes have been prepared by oxidizing copper meshes under alkaline conditions. This type of membranes showed an excellent performance in oil–water separation. Moreover, their productions are low-cost and easy to scale up, which are beneficial for industrial applications. Table 12 summarizes and compares the studies of modified membranes as mentioned above.

Table 12. Recent studies on functional material-modified membranes for wastewater treatment.

Authors (Year)	Materials Used	Outcomes
Zhou et al. (2010)	Zirconia particles	Effective treatment of oily wastewater, with fouling issues minimized.
Zhong et al. (2013)	Poly(methyl methacrylate) particles	Improved membrane performance.
Long et al. (2012)	Manganese oxide nanowires	Nanofibrous membrane is formed to show excellent capability in oil/water separation.

It is worth mentioning that the application of nanomaterials has greatly promoted the advance of recent membrane technology. Inorganic functional nanomaterials can be used to modify membranes, but they are insufficient in improving the anti-fouling, hydrophilic, and anti-compaction capabilities of the polymer membranes. Recently, a novel strategy of using inorganic functional nanomaterial with micro reaction locations (MLR) was investigated. This type of membranes can degrade organic and inorganic pollutants, as well as microbes through photocatalytic reactions enabled by catalysts such as titanium oxide or zirconium oxide solid superacids. In 2018, a review article was published by Zhang et al. [66], in which the recent progress of applying this type of functional materials in modifying membranes for wastewater treatment was summarized.

5. Application of Functional Materials in Polymer Sponges for Oil-Water Separation

Over the past few years, the studies of surface-modified polymer sponges have made significant advances and led to game-changing technologies for treatment of oily wastewater and oil spill cleanup. Polymer sponges such as polyurethane foams are commonly used cleaning materials in all kinds of domestic and industrial applications. Unlike traditional adsorbent materials (e.g., activated carbon, zeolites, clay, etc.), polymer sponges possess much larger pore sizes, faster adsorption rate, and higher uptake capacity. For these reasons, polymer sponges can easily overcome the challenges of clogged pores, slow adsorption, and poor re-usability, which are often encountered by conventional adsorbent materials.

Recently, surface-modified sponges have been developed in a rather innovative manner, exhibiting superior properties for crude oil droplets in water. For example, Cherukupally et al. [67] in 2020 developed a type of surface-engineered sponges (SEns) by coating polyester polyurethane (PESPU) sponges with nontoxic, earth-abundantly nanocrystalline silicon capped with decyl groups. Such modifications changed the surface properties of the sponges in terms of oleophilicity, charges, and roughness, which synergistically resulted in an excellent performance of adsorbing complex crude oil microdroplets in water at variable pH values. Experimental results showed that such modified sponges could remove oil microdroplets with efficiencies as high as 95–99%. The modified sponges also showed stable recyclability, suggesting great potential in large-scale recovery of crude oil microdroplets from wastewater.

In 2021, Cherukupally et al. [68] designed surface-modified polyester polyurethane sponges using nanosilicon and paraffin-like octadecyl ligands as surface modifiers. This type of wax-wetting sponges can adsorb oil droplets from wastewater between 5 °C and 40 °C with 90 to 99% removal efficacy for ten cycles. The adsorbed oil can be released in seconds by rinsing the sponges with heptol. Systematic investigations of the surface, rheological, adhesion, and thermoresponsive properties of the sponges have been carried out in their work, and the results pointed to promising application in cold water technology, such as removal of oil droplets from frigid waters.

Most recently (in 2022), another type of thermosetting polyurethane-nanosilicon sponge was reported by Cherukupally and co-workers [69]. This modified sponge showed stability at high temperature (up to 220 °C), and demonstrated a performance of reclaiming emulsified oily wastewater between 30 and 100 °C. It is noteworthy that the sponge achieved 92–96% removal efficiency for crude oil within 5 min. Like their previously reported wax-wetting sponges, this thermosetting sponge could readily release adsorbed oil by rinsing with heptol, showing excellent reusability. The remarkable performance of this functionalized polymer sponge makes it a promising high-temperature adsorbent for reclaim fracking effluents.

Sheng et al. [70] in 2021 modified a commercial melamine formaldehyde sponge with hyper-cross-linked polymers. The polymer coatings changed the wetting behavior of the sponge surface from hydrophilicity (pristine) to superhydrophobicity (modified), making the modified sponge useful for oil–water separation and recovery. In this work, polydimethylsiloxane (PDMS) was used as an adhesive agent, and a novel superhydrophobic/superoleophilic surface was developed on the sponge via direct surface condensation of dichloroxylene. Hierarchical rough surface structures were formed, resulting in increased surface areas, good physiochemical stability, high selectivity, and adsorption capacities for various types of oils and solvents. Ultrahigh separation efficiency (>99%) was observed for oil-in-water emulsions. The sponge also showed long-lasting durability and optimized surface wettability. It was reported that with suitable tuning of the pore sizes, the sponge could be applicable for treatment of oil droplets below 100 nm. This hyper-cross-linked polymer decorated sponge has a great potential in recovering decanted water at a permissible level.

In 2022, Gong and co-workers [71] reported the fabrication of a superhydrophobic sponge by dip coating a superhydrophobic polymer (SHMP-1) onto the skeleton of a melamine sponge. This modified sponge showed superhydrophobicity, large specific surface area, and high stability. It can be used to absorb light and heavy oil/organics with superior absorption capacities up to 38–105 times of its weight. The sponge can be recycled by squeezing (tested for 25 times). Furthermore, the separation efficiencies for both immiscible oil/water mixtures and oil-in-water emulsions were determined as above 99.5%. The authors claimed that this modified sponge is so far the strongest superhydrophobic absorbent for treating surfactant-stabilized oil-in-water emulsions. Clearly, the performance of this sponge bodes well for its real application in oil spill cleanup and separation of immiscible and challenging miscible oil-in-water mixtures. A summary and comparison of the recent studies on functional materials-coated sponges for wastewater treatment are outlined in Table 13.

Table 13. Recent studies on surface modifications of polymer sponges with functional materials for wastewater treatment.

Authors (Year)	Materials Used	Outcomes
Cherukupally et al. (2020)	Polyester polyurethane sponge coated with nanosilicon capped with decyl groups	Superoleophilic sponges that can efficiently remove crude oil microdroplets from water in a wide pH range.
Cherukupally et al. (2021)	Nanosilicon and paraffin coated polyurethane sponge	Excellent recovery oil droplets from extremely cold water, and easy reuse through heptol rinsing.
Cherukupally et al. (2022)	Thermosetting nanosilicon-coated polyurethane sponge	Recovery of emulsified oily wastewater in a wide temperature range. Suitability for high-temperature application.
Sheng et al. (2021)	Melamine formaldehyde sponge coated with cross-linked-polymers	Superhydrophobic/superoleophilic sponge surfaces suitable for removal of small oil droplets from water.
Gong et al. (2022)	SHMP-1 coated melamine sponge	The strongest superhydrophobic absorbent reported to date. Potential application in oil spill cleanup and spearation of various oil–water-emulsions.

6. Conclusions and Perspectives

Functional materials have been and are still being actively developed to promote the technological advances in wastewater treatment. As discussed in this review article, there are many challenges in this area, especially how to quickly and economically respond to massive-scale oil spills in various conditions. Development of effective methods for cleanup of oils on ocean surfaces or dispersed in water requires different strategies. Practical solutions can be found from the use of multiple functional materials as efficient adsorbents or the application of separation devices that are enabled/enhanced by novel functional materials, while the focus of this review is placed on the recent progress in wastewater treatment technologies, we are aware that there are still many relevant studies and reports in other fields, which are not included in this review but would be very useful for further advancement in the field of wastewater treatment. Our literature analysis has clearly shown that new functional adsorbent materials can be developed based on surface modifications of traditional adsorbent materials, ranging from biofilm carriers, sand, activated carbon, zeolite, clay, silica aerogel, to biopolymers and synthetic polymers. By changing the surface properties, such as roughness, porosity, hierarchical micro-/nano-structures, and wettability, these materials can be tuned to give unprecedented adsorptive performance that greatly expands their application in treating various pollutants in wastewater. Nanomaterials have been found to be highly useful coating materials for surface modifications. Nevertheless, their applications in technological development require extensive studies of the fundamental mechanisms and properties of various newly designed nanomaterials. Production costs, easiness to use, and environmentally friendliness should be taken into serious consideration, when new functional materials and technologies are developed for wastewater treatment. In this vein, functional materials derived from green and sustainable sources (e.g., biomass, biopolymers, agricultural wastes) deserve more active studies. Moreover, many real applications have special requirements for compatibility, selectivity, and adaptivity. To address these issues, multifunctional materials, such as those possess both adsorption and catalytic properties for self-cleaning, are advantageous and hence call for more research attention. Separation devices such as superhydrophobic and superhydrophilic meshes, membranes, and sponges represent a new frontier in this area. Recent advances as discussed in this review are quite exciting. It is worth noting that the application of functional materials in advanced separation technologies has led to very successful methods for wastewater treatment under harsh conditions. Continued research activities and technological developments in all the above-mentioned directions are expected to revolutionize the current industrial undertakings and greatly contribute to the global efforts for environmental control and protection.

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