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Review

Prospects for Combined Applications of Nanostructured Catalysts and Biocatalysts for Elimination of Hydrocarbon Pollutants

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Featured Application: The information presented in the review allows us to highlight the most successful scientific developments and general trends in the development of current research in the field of the use of effective technologies for the elimination of hydrocarbon pollutants or purification of oil-polluted wastewaters based on the combined use of nanocomposites, nanocatalysts and biocatalysts, allowing us to improve the target results and obtain a synergistic effect.

Abstract: Due to the presence of environmental problems, it is urgent to improve the processes aimed at the processing and purification of hydrocarbon-containing wastes and wastewaters. The review presents the latest achievements in the development of nanostructured catalysts made from different materials that can be used to purify oil-polluted wastewaters (petroleum refinery wastewater, oilfield-produced water, sulfur-containing extracts from pre-oxidized crude oil and oil fractions, etc.) and eliminate components of hydrocarbon pollutants (polyaromatic hydrocarbons, phenols, etc.). The results of the analysis of possible combinations of chemical and biological catalysts for deeper and more effective solutions to the problems are discussed. The possibilities of highly efficient elimination of hydrocarbon pollutants as a result of the hybrid application of nanoparticles (graphene oxide, mesoporous silica, magnetic nanocatalysts, etc.) or catalytic nanocomposites for advanced oxidation processes and biocatalysts (enzymes, cells of bacteria, mycelial fungi, phototrophic microorganisms and natural or artificial microbial consortia) are analyzed.

Keywords: nanocatalysts; nanocomposites; hydrocarbon pollutants; oil-containing wastewater; degradation; oxidation; biocatalysis; hybrid process

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1. Introduction

In the 21st century, industries related to the extraction, transportation, storage, processing and use of hydrocarbon raw materials continue to actively develop. Various wastewaters of oil-producing, oil-refining, chemical, transporting and other fields of industry form multi-tonnage effluents containing residual concentrations of hydrocarbons [1–4]. The volume of oilfield-produced water (OPW) alone is on average at least 250 million barrels per day worldwide [2,5,6]. Crude oil emulsions and hydrocarbon-contaminated wastewaters and soils are considered sources of potential threat to the environment and living objects [7].

Polyaromatic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene, and xylenes (BTEX) usually predominate among dissolved organic compounds in hydrocarbon-containing wastes [8].

Hydrocarbon-containing wastewaters may contain various toxic organic compounds: aromatic substances, MTBE (methyl tert-butyl ethers), naphthenic acids, methanol, ketones, ethers, brominated organic compounds, estrogens, PCBs (polychlorinated biphenyls), phthalates, linear alkyl benzene sulfonates, furans and others [1,4,9,10]. However, BTEX are rarely considered due to their high volatility and rapid decomposition in water as a

source of serious ecotoxicological effects. It is believed that phenols and PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene and others) pose the greatest danger to the environment and human health. Alkylphenols, especially with long (C7–C9–carbon) chain, and naphthenic acids can have a significant negative effect on the endocrine system, causing estrogenic effects in vertebrates [6,11].

Today, the effective use of chemical, physical–chemical and biological approaches to the purification of hydrocarbon-containing liquid effluents is known (Figure 1). Physical methods using gravity separators, hydrocyclones and reactors with flocculants are applied at the first stage for the primary processing of oily wastewaters and separation of suspended particles [12]. Then, deeper secondary and tertiary stages of purification based on a combination of various physical–chemical (freezing/thawing, membrane treatment, adsorption, oxidation, etc.) and biological methods are carried out [13].

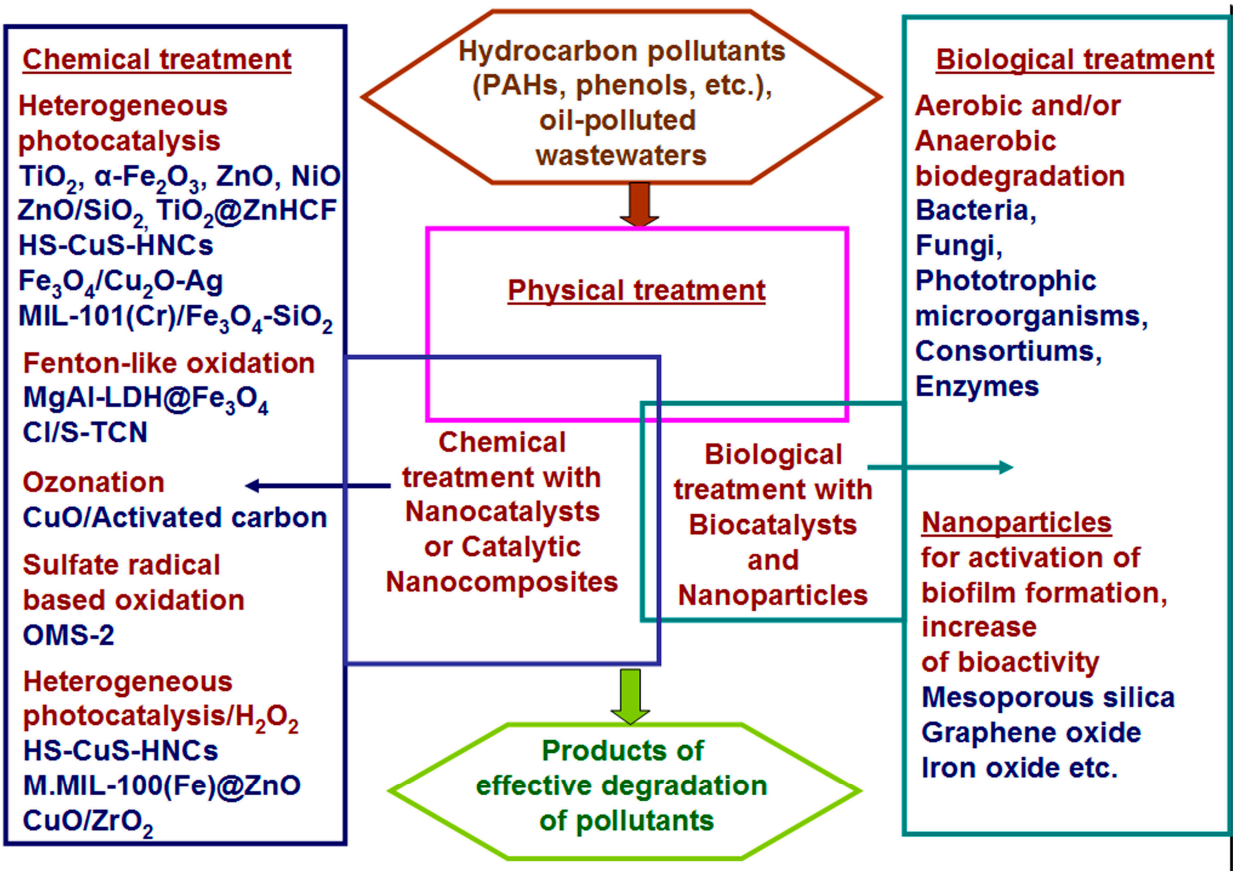

Figure 1. Different catalysts and processes based on their use in the treatments of oil-containing wastewaters.

Aerobic, anaerobic and hybrid bioreactors are actively used for the process of elimination of hydrocarbon pollutants [1]. Anaerobic biocatalytic conversion allows a part of the energy potential of hydrocarbon-containing wastewaters to be used in the form of accumulating biogas. At the same time, toxic hydrocarbons can inhibit the activity of methanogens and microbial processes with their participation [14]. At high concentrations of hydrocarbons in the utilization of waste, prior to their introduction into the bioreactor, it is advisable to carry out preliminary physical–chemical treatment, which ensures the rapid destruction of molecules that are difficult to biotransform [1]. The combinatory treatments involving physical and/or biological and chemical treatments not only provide the effective transformation of pollutants but also allow the conservation of resources and the energy contained in them [4].

As a rule, the purpose of catalytic treatment of polluted media is to reduce the level of their contamination to the limits permissible for their discharge. Due to the complex chemical composition, high concentrations and stability of polluting components, it is difficult for existing purification systems of hydrocarbon-containing wastes and wastewaters to ensure that the results obtained meet the strict requirements imposed on them. In this regard, the search for new effective approaches to the elimination of hydrocarbon pollutants remains relevant. Due to the active development of chemical science in the direction of the creation of novel nanomaterials and nanostructured catalysts, a major breakthrough has recently been made in the development of chemical catalysis, which provides, mainly owing to oxidative reactions, effective pretreatment of hydrocarbon-containing wastes. Heterogeneous catalysts in the form of nanoparticles (NPs) are usually characterized by a high ratio of their surface area to the volume they occupy. This leads to their higher efficiency of action with the simultaneous possibility of separation from the reaction medium after application [15,16].

This review presents an analysis of current trends in the development of nanostructured catalysts and applications in the conversion of hydrocarbon-containing wastes. The review is also aimed at analyzing the probable combination of chemical catalysis with biocatalysts (BCs) for deeper and more efficient processing of hydrocarbon-containing wastes (Figure 1). The latest achievements (2017–2023) in the field of advanced oxidation processes using NCs and NComs developed for the decomposition of hydrocarbon pollutants were used as the main objects of analysis in this review. Possible options for biocatalytic treatment of various hydrocarbon pollutants using homogeneous or immobilized BCs (including biofilms) and combinations of various BCs with nanomaterials were also compared in this review. Some mechanisms associated with the manifestation of a synergistic effect in the action of various catalysts were especially emphasized.

2. Nanocatalysts and Nanocomposites in Pretreatment Processes from Carbon-Containing Real or Model Waste and Contaminated Wastewater

Today, the main directions of chemical degradation of hydrocarbon-containing wastes using nanocatalysts (NCs) and catalytically active nanocomposites (NComs) are associated with advanced oxidation processes (AOPs) (Table 1) [15–32] and correspond to general trends in the development of processes related to wastewater treatment [33].

AOPs are based on the oxidation of components of purified media under the action of radicals, such as hydroxyl (•OH), superoxide ($\bullet O_2^-$) and sulfates radicals ($SO_4^-\bullet$). Among the varieties of AOPs used for wastewater and soil treatment, there are photocatalytic oxidation, Fenton-like oxidation, electrochemical oxidation, wet air oxidation, ozonation, and oxidation with H_2O_2, ultrasound, microwave or gamma irradiation activation, sulfate radical-based advanced oxidation processes and their combinations [33]. Due to the development and application of NCs and NComs in the implementation of AOPs in the processes of degradation of hydrocarbon pollutants, significant results have been achieved in almost all of these areas in recent years (Table 1). The prospects of the practical application of NCs are increased due to the possibility of their repeated use (3–10 cycles) [15,16].

The method of photocatalytic oxidation has become the most widespread due to the availability of reagents, high efficiency, environmental friendliness and relatively low energy consumption compared to other physico-chemical methods. Among the NCS for photooxidation are TiO_2, ZnO, ZrO_2, α-Fe_2O_3, MgO_3, CeO_2, SnO_2, WO_3, CuS, ZnS, WS_2, CdSe, CdS, MgS_2, bi-based materials (composite Bi_2WO_6/CN and ribbon-like oxygen-rich $Bi_{12}O_{17}Cl_2$) and Ag_3PO_4 in combination with metal oxides (Mn_3O_4/MnO_2-Ag_3PO_4 and Ag_3PO_4@Fe_3O_4) [34–36]. In a number of processes related to the heterogeneous photocatalytic purification of water and soil from organic pollutants, NCs from the mentioned list are also used [15,17,21–23,25,31,32].

Table 1. Advanced oxidation processes with NCs and NComs for degradation of hydrocarbon pollutants *.

NCs/NComs; Size (nm) [Reference]	Pollutants	Reaction Conditions	Removal Efficiency (%)
Heterogeneous photocatalysis			
TiO_2 (30 nm) [17]	Phenol (300 ± 7 mg/L), soap oil and grease (SOG) (4000 ± 23 mg/L) in oil refinery wastewater	8 g/L of catalyst, aeration flow rate of 1.225 L/min, 90 min	76% of phenol and 88% of SOG
TiO_2 (44.3–48.0 nm) [18]	Anthraquinone (0.5 mg/L)	200 mg/L of catalyst, solar irradiation 100 mW/cm^2, 240 min	57%
Haematite (α-Fe_2O_3) [19]	Petroleum refinery wastewater COD 1257 mg/L	pH 7.5, 1.494 g/L of catalyst, H_2O_2/COD ratio of 1 mg/mg, UV-A lamp solar irradiation, 90 min	90.85% of COD
ZnO or NiO [20]	Anthracene (101.8 mg/L)	pH 7.2, 55.6 mg/L of catalyst, emulsion solution—230 min, anthracene aqueous ethanol solution—280 min	90% with ZnO and 87% with NiO for anthracene emulsion solution; 81% with ZnO and 86% with NiO for anthracene aqueous ethanol solution
ZnO nanorods 2.11 ± 0.32 μm length and 96.26 ± 11.13 nm diameter [21]	Phenol (10 mg/L)	pH 5, visible light 1000 W/m^2, 5 h	84.3%
ZnO/SiO_2 with Palash leaves extract (3–35 nm) [22]	Acenaphthylene (176 mg/L), COD (497 mg/L) in petrochemical wastewater	1 g/L of catalyst, 30 °C, visible light, 4 h	79% of Acenaphthylene, 70% of COD
HS-CuS-HNCs Hierarchically structured CuS hollow nanocatalyst [15]	Petroleum refinery wastewater (COD 380 mg/L)	pH 7.6, 1 g/L of catalyst, 180 min, 10 cycles	about 66% of COD
TiO_2@ZnHCF Titanium dioxide based zinc hexacyanoferrate framework nanocomposite (100 nm) [23]	Tricyclic PAHs: acenaphthene, phenanthrene and fluorine (2 mg/L)	Neutral pH, 15 mg/L of catalyst, sunlight, 6 h	93–96% from water, 82–86% from soil, 81.63–85.43% from river sediment
Fe_3O_4/Cu_2O-Ag nanocomposite (5 nm) [24]	PAHs: naphthalene (5 mg/L), benzo(a)pyrene (5 mg/L), anthracene (5 mg/L)	0.5 g/L of catalyst, visible light, 60–180 min	80–90%
MIL-101(Cr)/Fe_3O_4-SiO_2 (35% of Fe_3O_4-SiO_2) Superhydrophobic composite (400/80–120 nm) [25]	Synthetic and real oilfield-produced water (TPH 170 mg/L, COD 550 mg/L)	pH 4, 0.5 g/L of catalyst, visible and UV light, 150 min	97.7% and 99.2% of TPH, 95.17% and 96.6% of COD from real and synthetic OPW, respectively
Fenton-like oxidation process			
Nanoscale zero-valent iron (nZVI), commercial (50 nm) [26]	Water from oil and gas exploration site (15 different PAHs present in real water samples; Naphthalene (201.46 μg/L) and benzo(g,h,i) perylene (23.15 μg/L)	pH 2.94, 4.35 g/L of nZVI, 1.60 g/L of H_2O_2, 199.90 min	89.5% and 75.3% of PAHs and COD, respectively
MgAl-LDH@Fe_3O_4 [27]	Concentrated liquor of gas field wastewater (refractory organic pollutants)	pH 5, heterogeneous electro-Fenton system, 4 h	88.18% for COD
Cl/S-codoped carbon nitride nanotube clusters (Cl/S-TCN) [28]	Oilfield-produced water	pH range 3–9, metal-free photo-Fenton, 10 mM H_2O_2	82.6% for COD

Table 1. *Cont.*

NCs/NComs; Size (nm) [Reference]	Pollutants	Reaction Conditions	Removal Efficiency (%)
Ozonation			
CuO/Activated carbon (250~350 nm) [29]	Heavy oil refinery wastewater (oil 78 mg/L, COD 2950 mg/L)	pH 7.3, 5.0 g of catalyst, 90 mg/L of O_3, 75 min	94.2% of COD 89.7% of oil
Sulfate radical-based oxidation			
OMS-2 Manganese oxide octahedral molecular sieve nanorods [16]	PAH: phenanthrene (1.0 mg/L) in water and sewage	pH range 4–11, 0.1 g/L of catalyst, peroxomonosulfates 6 mmol/L, room temperature, 360 min, 3 cycles	>99%, 68%, 82% and 79% from model wasterwater, tap water, Yellow river and Qinghai lake, respectively
Hybrid chemical processes with nanocatalysts			
HS-CuS-HNCs Hierarchically structured CuS hollow nanocatalyst [15]	Petroleum refinery wastewater (COD 380 mg/L)	Heterogeneous photocatalysis/H_2O_2 pH 7.6, 1000 mg/L of catalyst, 3000 mg/L of H_2O_2, room temperature, solar-light, 2 h	98% of COD
M.MIL-100(Fe)@ZnO [30]	Phenol (5 mg/L), Biphenol A (5 mg/L), Atrazine (5 mg/L)	Heterogeneous photocatalysis/H_2O_2 pH 2, 0.2 g/L of catalyst, 10 mM H_2O_2, room temperature, 2 h	95% of Phenol, 95% of Biphenol A, 85% of Atrazine
CuO/ZrO_2 nanocomposite 40.32 nm [31]	Marine diesel (100 mg/L)	Heterogeneous photocatalysis/H_2O_2 0.5 g/L of catalyst, 400 °C, 0.3 g/L of H_2O_2, visible light, 6 h	96.96%
Cu-based perovskite oxides (La_2CuO_4) [32]	Petroleum refining wastewater (COD 3800 mg/L TOC 1259 mg/L)	Wet air oxidation processes/H_2O_2 pH 7.5–8.0, 0.75 g/L of catalyst, 7 mL/L of 30% H_2O_2, 100 °C, 0.5 h	89.58% of COD, 87.38% of TOC

* COD—chemical oxygen demand; MIL—Materials of Institute Lavoisier; MIL-101(Cr)—metal–organic frameworks (MOFs) based on chromium (III) and polymeric terephthalate; M.MIL-100(Fe)—mesoporous metal–organic framework based on iron (III) carboxylate; OPW—oilfield-produced water; PAHs—Polycyclic aromatic hydrocarbons; PRW—petroleum refinery wastewater; SOG—soap oil and grease; TiO_2@ZnHCF—Titanium dioxide based zinc hexacyanoferrate framework; TOC—Total organic carbon.

The crystal structure of the catalyst plays an important role in the efficiency of its functioning. Compared to a bulk-size CuS catalyst, hierarchically structured CuS hollow nanocatalyst HS-CuS-HNCs with a narrower band gap (Eg = 0.96 eV) exhibited characteristics of strong visible light absorption, highly enhanced quantum efficiency and large specific area (101.5 m^2/g). HS-CuS-HNCs showed significantly enhanced activity for the degradation of pollutants under both artificial and real solar light sources. About 66% of COD in PRW was removed in 3 h within the degradation process in the presence of a 1.0 g/L nanocatalyst and pH 7.6 [15].

NComs, in comparison with NCs, show higher activity due to their increased active surface area. Activated carbon, graphite carbonitrides g-C_3N_4, Bi_2WO_6, three-dimensional graphene gels, MOFs and others are tested as carriers for obtaining NComs, with the possibility of loading a large number of NCs. A tendency to increase the efficiency of degradation of pollutants was revealed for NComs such as TiO_2@ZnHCF compared with TiO_2 [23], and for activated carbon-supported copper (II) oxide CuO/AC, better results were found in comparison with CuO [29]. MOFs and their derivatives become an integral part of heterogeneous catalysts in the mineralization of organic substances due to their large specific surface area, large number of active centers and simplicity of structural regulation [25,30].

When combining different AOPs, a synergistic effect can be expected. The activity of hierarchically structured CuS hollow nanocatalyst HS-CuS-HNCs was drastically enhanced further in the presence of hydrogen peroxide (H_2O_2) (98% of COD was removed in 2 h in PRW in the presence of 1.0 g/L catalyst, 3.0 g/L H_2O_2 and pH 7.6). This was attributed to the synergistic effect between HS-Cs-Hns and H_2O_2, leading to the enhanced quantum efficiency and production of more reactive oxygen species [15]. The highest efficiency (89.58–98%) of wastewater cleaning with minimal time (0.5–2 h) is observed when combinations of NCs are used [15,30–32].

An increase in the concentration of the oxidants and the doses of NCs are expected to increase the efficiency of removing organic pollutants [37,38].

In the course of wastewater treatment from organic pollutants, the presence of some cations and anions in the medium in combination with the oxidizer used and a certain structure plays an important role. The salinity of water (1–4% NaCl) had practically no effect on the efficiency of photocatalytic decomposition of phenolic derivatives with ZnO nanorods. Single- and divalent cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) had little effect on the process. The presence of Cl^- and SO_2^{2-} anions in the medium contributed to an increase in the rate of degradation of pollutants with high efficiency (85.1% and 88.0%, respectively). In the presence of CO_3^{2-} and Br^- anions, the efficiency of the processes decreased to 35.5% and 14.7%, respectively [21]. The inhibitory effect of anions in the decomposition of fenantren with manganese oxide octahedral molecular sieve nanorods during sulfate radical-based oxidation was highest in the presence of NO^{2-} and PO_4^{3-} ions, followed by Cl^-, NO_3^- and CO_3^{2-}, and the lowest was with HCO_3^- [16].

As for the comparative analysis of the known data on the decomposition of the specific pollutants considered in this review, when comparing ZnO and TiO_2, TiO_2 is more effective for the photocatalytic decomposition of phenol. The estimated decomposition rates of phenol in the presence of TiO_2 and ZnO are ~2.5 mg/L/min [17] and ~0.03 mg/L/min [21], respectively. The inclusion of ZnO in the NComp of the M.MIL-100(Fe)@ZnO provided a slight improvement in the decomposition rate (~0.04 mg/L/min) [30], but it did not radically change the situation.

The loading of catalysts α-Fe_2O_3, HS-CuS-HNCs or La_2CuO_4 (0.75–1.5 g/L) into petroleum-refining wastewater (PRW) [15,20,32] during its purification provides the best results in COD removal.

For the destruction of PAHs in comparison with other pollutants (Table 1), the lowest process rates were noted: ~0.001 mg/L/min for anthraquinone with TiO_2 [18], ~0.3 mg/L/min for anthracene with ZnO [19] or with Fe_3O_4/Cu_2O-Ag [24] and ~0.3 mg/L/min for acenaphthylene with ZnO/SiO_2 [22].

It should be noted that almost all processes with NCs presented in Table 1 proceed at a pH close to neutral [15,19,20,23,29,32] or slightly acidic [21,27] values and at ambient temperatures, which is important if a further combination of these processes with biocatalytic reactions is assumed. For sulfate radical-based oxidation of phenanthrene in the presence of manganese oxide octahedral molecular sieve nanorods, equally high purification rates of model and real liquid media were achieved at pH 4–11 [16].

The same trend was noted for metal-free photo-Fenton Cl/S with co-doped carbon nitride nanotube clusters (Cl/S-TCN) during oilfield-produced water purification at pH 3–9 [28]. However, the pH value may have an impact on the effectiveness of AOPs in some cases [21,25,26,30]. It was shown that the photocatalytic decomposition of phenol in the presence of ZnO at pH 5 reaches 84.3%, and as the pH increases, the efficiency decreases uniformly, reaching 69.4% at pH 9 [21].

In favor of carrying out processes at pH 2–4, the researchers chose to decompose phenol, biphenol A and atrazine with M.MIL-100(Fe)@ZnO during heterogenic photocatalysis/H_2O_2 [30] of PAHs (naphthalene and benzo(g,h,i)perylene) present in wastewater from oil and gas exploration sites. That was performed with nZVI during the Fenton-like oxidation process [26] and with MIL-101(Cr)/Fe3O4-SiO_2 during the photocatalysis [25] for the treatment of oilfield water.

Among the processes that differed from AOPs, pyrolysis is known as an approach to the destruction of organic pollutants using NCs [34]. The successful decomposition of oily sludge by $ZnFe_2O_4$ (NPs = 30 nm) during three-stage pyrolysis with the activation of NCs by microwaves was shown. The high energy intensity and the realization of some individual stages of the process at high temperatures (up to 300 °C) should be noted among the disadvantages of this process.

It was noted that the preliminary chemical treatment of hydrocarbon contaminants using AOPs provides better biodegradation of the resulting products at the subsequent biocatalytic processing stage [35].

Microalgae can be used as bioindicators of the biotoxicity of NCs in real natural systems [36]. It appeared that *D. tertiolecta* cells had high enough sensitivity to paraffins (6.9% $C_{10}H_{22}$, 33.1% $C_{11}H_{24}$, 34.1% $C_{12}H_{26}$, 25.4% $C_{13}H_{28}$, and 0.4% $C_{14}H_{30}$) when *C. vulgaris* cells were more sensitive to NPs of ZnO (80–200 nm). At the same time, the combination of microalgae and NPs provided a synergistic effect and increased the efficiency of degradation of hydrocarbon pollutions of the treated media.

It is precisely such effects that attract the maximum interest of researchers at the present stage of scientific development in solving environmental problems. In this regard, recently, the possibilities of using combinations of various microbial cells as BCs possessing various enzymatic activities with nanomaterials in the purification processes of hydrocarbon-containing wastewaters and soils have been actively investigated.

3. Prospects for the Use of Biocatalysts with Nanostructures and Nanomaterials in the Purification Processes

It is known that in the stages of biological wastewater purification from organic pollutants, different types of microbial biocatalysts (BCs) are used (Table 2) [37–68], in the role of which bacterial cells [37,38,41–44,63,65,66], filamentous fungi [39,51] or phototrophic microorganisms [40,53] are most often used (Figure 2).

At the same time, various bioreactors are actively used to maintain both aerobic and anaerobic conditions for the destruction of pollutants under the action of microbial BCs.

Today, not only microbial cells are being studied among BCs, but also NCs of biological origin, which are microbial enzymes that are proposed for use in the destruction of hydrocarbon pollutants, including in the content of created NComs [69].

From a practical point of view, it is more expedient to introduce individual enzymatic NCs into purification systems not alone but as components of whole microbial cells synthesizing these enzymes.

Table 2. Biocatalytic treatments of various hydrocarbon pollutants.

Biocatalyst [Reference]	Pollutants	Conditions and Degradation Efficiency
	Homogenous BCs	
Achromobacter xylosoxidans [37]	Pyrene 100 mg/L	pH 7–9, 37–40 °C, 0–2.5% NaCl, 15 days, 50% of of pyrene
Halomonas shengliensis [38]	Pyrene 50 ppm	25 °C, 10 g/L NaCl; 50% degradation
Penicillium sp. [39]	Crude oil 1% (*v*/*v*)	14 days, 30 °C; 57% degradation
Chlorella vulgaris [40]	Oilfield-produced water (7 mg total hydrocarbons/L) and crude oil (32 mg total hydrocarbons/L)	5 days, 20 °C; 36.8 ± 4.2 µmol photons/m^2/s 28.5% degradation from oilfield-produced water; 34.3% degradation from crude oil
Rhodocccus erythropolis or *Pseudomonas stuzeri* [41]	PAHs (332.2 mg/kg soil)	Slurry Bioreactor, 28 °C, pH 8.2; 8 mg/L dissolved oxygen, 15 days, 70–80% degradation
Brevibacillus brevis [42]	Naphthalene and pyrene (100 mg/L)	pH 5.0, 25 °C, 18 days, 80% of naphthalene
Proteus mirabilis [42]		pH 5.0, 25 °C, 18 days, 94% of naphthalene
Rhodococcus quinshengi [42]		pH 5.0, 37 °C, 18 days, biodegradation: 94% of naphthalene, 56% of pyrene
R. ruber Ac-1513 D and *R. erythropolis* Ac-1514 D [43]	Petroleum hydrocarbons 446.7–526.8 g/kg dry soil	Aerobic-anaerobic bioremediation method with 10^8 cells/mL; nitrate salt is used as electron acceptor on area 25 × 30 m^2 3 times with a 3-week interval; 20–30 °C; 63 days; Degradation of saturated, aromatic and resin-asphaltene was 72.6%, 66.5% and 57.2%, respectively.
R. ruber Ac-1513 D and *R. erythropolis* Ac-1514 D [44]	Oil products 482 g/kg dry soil (48%)	Hydrolysis of the bituminous crust by calcium hydroxide (2%) 3 times with a 3–4-day interval; bioremediation with *Rhodococcus* strains (10^6 cells/mL) was conducted 3 times with a 7-day interval; 20–30 °C, pH 7.8; 33 days for 26.4–48.2% degradation of oil pollution
R. ruber Ac-1513 D and *R. erythropolis* Ac-1514 D [45]	Oil products 98 g/kg dry soil (9.8%)	Anaerobic bioremediation, 10^9 cells/mL electron acceptor $Ca(NO_3)_2$; 1.25%, 28 °C, pH 7.8; 10 days; potential degradation of the oil pollution 90% for 90 days
Extremophilic consortium: *Ochrobactrum*, *Bacillus*, *Marinobacter*, *Pseudomonas*, *Martelella*, *Stenotrophomonas* and *Rhodococcus* [46]	Low-molecular-weight (LMW) petroleum hydrocarbons (200 ppm) such as anthracene, phenanthrene, fluorene and naphthalene	Soil, 8% salinity, pH 10, 60 °C, 8 days, 100% degradation efficiency
	High-molecular-weight (HMW) hydrocarbons such as pyrene (100 ppm), benzo(e)pyrene (20 ppm), benzo(k)fluoranthene (20 ppm) and benzo(a)pyrene (20 ppm)	Soil, 8% salinity, pH 10, 60 °C, 8 days, 93%, 60%, 55% and 51% degradation
Consortium: *Campylobacter hominis*, *Bacillus cereus*, *Dyadobacter koreensis*, *Pseudomonas aeruginosa*, *Micrococcus luteus* [47]	Bonny light crude oil	2% (*v*/*v*) crude oil, 30 °C, 21 days 73% degradation
Consortium of genus *Pseudomonas*, *Methylobacillus*, *Nocardioides*, *Achromobacter*, *Methylophilaceae*, *Pseudoxanthomonas*, *Caulobacter* [48]	The final concentration of total PAHs from coal and petroleum was 97.63 mg/ kg dry weight soil	35 days, 25 °C, in soil; 75% PAHs

Table 2. *Cont.*

Biocatalyst [Reference]	Pollutants	Conditions and Degradation Efficiency
Halophilic bacterial consortium [49]	PAHs	12 days, pH 7.4, 40 g/L NaCl concentration low-molecular-weight (above 90% for phenanthrene and fluorene) and high-molecular-weight (69 ± 1.4 and 56 ± 1.8% at 50 and 100 mg/L of pyrene) polycyclic aromatic hydrocarbons (PAHs)
Benthic diatom-associated bacteria [50]	3 µg/L Benzo(a)pyrene and 265 µg/L fluoranthene	7 days, 88% of fluoranthene, 79% of Benzo(a)pyrene
Consortium: *Aspergillus niger*, *Aspergillus sydowii*, *Fusarium lichenicola* [51]	101.7 mg/L PAHs in oilfield wastewater	21 days, 85.2% degradation (with 100% naphthalene and chrysene)
Consortium of *Chlorella* sp. and *Rhodococcus wratislaviensis* with preliminary adaptation [52]	Mixture of 50 mg/L phenanthrene, 10 mg/L pyrene, 10 mg/L benzo[a]pyrene	24 °C, 200 µmol photons/m^2/s, 150 rpm, 21 days 100% degradation
Nannochloropsis oculata or *Isochrysis galbana* with preliminary adaptation [53]	Oilfield-produced water (270 mg oil/L)	pH 7.2, 25 ± 1 °C, light photoperiod—18:6 (2000 lux); 66.5–68% degradation
Immobilized BCs including self-immobilized systems (biofilms)		
Bacterial consortium immobilized in magnetic floating biochar gel beads [54]	Pyrene (20 mg/L), benzo(*a*)pyrene (10 mg/L), indeno(1,2,3-*cd*)pyrene (10 mg/L)	Seawater, pH 8.1, 30 °C, 30‰ salinity, 16 days. Biodegradation: 89.8%, 66.9% and 78.2% of PYR, BAP and INP, respectively
Biofilm and pellets of consortium (key functional genera: *Rhodobacter*, *Citreibacter*, and *Roseovarius*) [55]	Oilfield-produced water (6.38 ± 2.31 mg oil/L)	multistage bio-contact oxidation reactor, pH 7.5–8.1, 45–50 °C, 44.07% oil degradation
Microbial mats (cyanobacteria and bacteria) [56]	Oilfield-produced water (4.3 ± 1.0 mg of the C_{10} to C_{30} alkanes/g mats)	28 days, 30 °C, 50 rpm, pH 8.5, 18 ppt salinity, with partially hydrolyzed polyacrylamide; 41–49% degradation
Active sludge [57]	Synthetic produced water (255 mg oil/L)	Aeration tank, 3.5 L/min air, pH 6.0, 7 days; 51 g/L sodium chloride, 99.01 ± 0.28% degradation
This system contained dissolved air flotation (DAF), yeast bioreactor (yeast immobilized on policyurepan), upflow anaerobic sludge blanket reactor (UASB), and biological aerated filter [58]	Oilfield wastewater (145 mg oil/L)	60 days, 99.6% oil degradation
Native halophilic bacterial consortium immobilized on walnut shell [59]	Synthetic oilfield-produced water (191 mg/L oil)	48 days, moving bed biofilm reactor, 97.8% oil degradation
Methanogenic culture derived from a high-temperature oil reservoir production water [60]	Paraffinic n-alkanes (C22–C30)	97% degradation and biogas accumulation, 736 days

Table 2. *Cont.*

Biocatalyst [Reference]	Pollutants	Conditions and Degradation Efficiency
Consortium immobilized in cryogel of poly (vinyl alcohol): AC1 (80% anaerobic sludge plus 10% *Desulfovibrio vulgaris* plus 10% *Clostridium acetobutilycum*) for the straight-run gasoline fraction (Nafta) and AC3 (70% anaerobic sludge plus 10% *D. vulgaris* plus 10% *C. acetobutilycum* plus 5% *Rhodococcus ruber* plus 5% *Rhodococcus erythropolis*) for the straight-run diesel oil raction, non-hydrotreated vacuum gas oil, gas condensate, and crude oil [61]	Sulfur-containing extracts from pre-oxidized crude oil, non-purified vacuum gas oil, straight-run gasoline fraction (Naphtha), gas condensate and straight-run diesel fraction (7–10 g/L COD)	Biotransformation in methanogenic anaerobic reactor, 100% conversion of S-organic compounds to inorganic sulfide or biomass, biogas accumulation with 68–76% of CH_4 for 20 days
Consortium immobilized in cryogel of poly (vinyl alcohol): AC6 (80% anaerobic sludge plus 10% *Rhodococcus opacus* plus 10% *Desulfovibrio desulfuricans*) [62]	Sulfur-containing extracts from pre-oxidized crude oil and oil fractions with hydrolysates of chicken manure and *Chlorella vulgaris* biomass (6.4–16 g/L COD)	Biotransformation in methanogenic anaerobic reactor, 100% conversion of S-organic compounds to inorganic sulfide or biomass, biogas accumulation with greater than 70% of CH_4 for 6–42 days
Consortium immobilized in cryogel of poly(vinyl alcohol): AC6 (80% anaerobic sludge plus 10% *R. opacus* plus 10% *D. desulfuricans*) and AC7 (90% adapted DEAMOX sludge plus 10% anaerobic sludge) [62]	Sulfur-containing extracts from non-purified vacuum gas oil with hydrolysates of chicken manure and *Chlorella vulgaris* biomass (6.4 g/L COD)	The two-stage biotransformation in methanogenic anaerobic reactor (MAR) and denitrifying ammonium oxidation (DEAMOX) reactor; 100% conversion of S-organic compounds to inorganic sulfide or biomass, biogas accumulation with 70% of CH_4 for 20 days
	Combination of BCs with nanomaterials	
S. aestuarii 357 [63]	Naphthalene (0.128 mg/L)	Two stages: (1) the formation of the naphthalene@FeNP-NDI-DA complex with FeNP-NDI-DA nanoparticals; (2) addition of *S. aestuarii* 357; 100% biodegradation
Brevibacillus parabrev 1.13×10^8 cells/mL [64]	Oily wastewater: Tetradecane 3%	Magnetic NPs of Fe_3O_4 (10 nm) 76% tetradecane was degraded by cells for 15 days
Halamonas sp., *Vibrio gazogenes* or *Marinobacter hydrocarbonoclasticus* [65]	Crude oil (375 mg/L)	Polyvinylpyrrolidone (PVP)-coated iron oxide NPs (11.2 nm) 100% oil degradation for 24–48 h
M. hydrocarbonoclasticus [66]	Crude oil (0.5% *w*/*v*)	Facile chemical modification of mesoporous silica NPs (mSNPs) (10 nm) 100% oil degradation for 45 days
Bacillus cereus 1.55×10^5 cells/mL [67]	PAHs: Anthracene, phenanthrene	Graphene oxide quantum dots (GOQDs) 52.7% degradation of PAHs for 3.5 days (1.7% degradation in control sample)
Consortium in membrane bioreactor [68]	Petroleum refinery wastewater (52.2 mg/L COD)	Membrane bioreactor (MBR)-H_2O_2/UV Hybrid pretreatment before nanofiltration 80% of COD degradation for 1 h

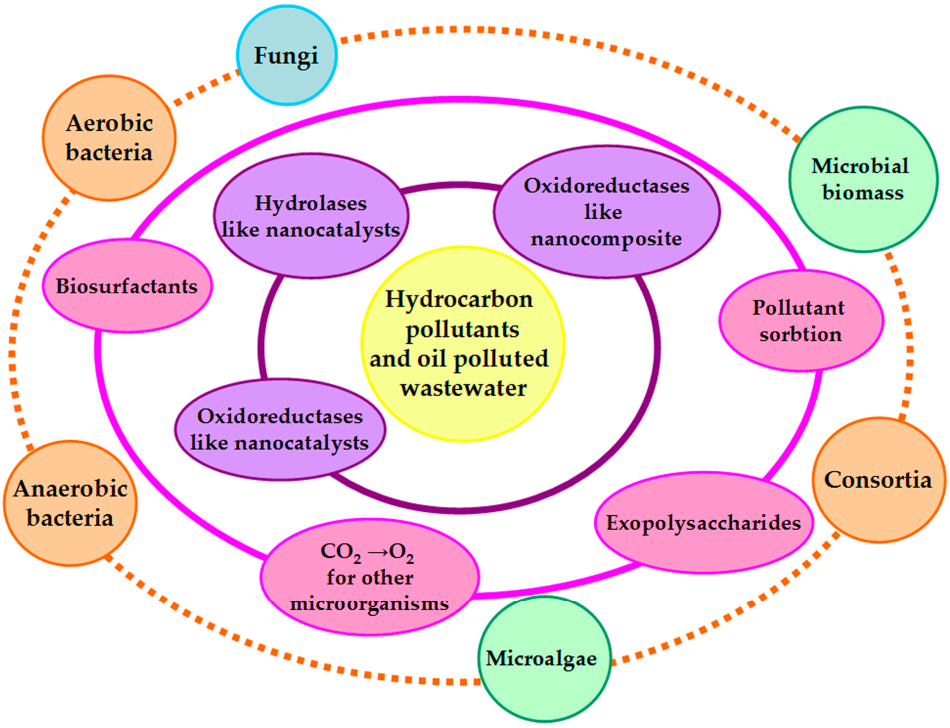

Figure 2. Various BCs used for the degradation of hydrocarbon pollutants and wastewaters polluted by oil residues discussed in the review. The direct effect on hydrocarbon pollutants is provided by enzymes that are NCs (marked by violet). These enzymes can be synthesized by microbial catalysts directly in the process of destruction, as well as isolated and used as parts of NComs. The outer contour contains a set of the most commonly used microbial BCs: bacteria and consortia (marked by orange), mycelial fungi (marked by blue) and phototrophic microorganisms and those microbial cells that are not effective destructors of hydrocarbon pollutants but act as auxiliary "personnel" in such processes (marked by green).

Not all microbial cells secrete synthesized enzymes into the environment. Thus, the stage of their isolation for use in the processes of destruction of hydrocarbon pollutants makes a significant contribution to the increase in the costs of the process with the participation of enzymatic NCs.

The presence of BCs in the form of living whole cells of microorganisms ensures the presence of a constant source of replenishment of enzymes in the system. They can be synthesized in cells when they are present in media with hydrocarbon pollutants as inductors.

Microorganisms, especially those that are parts of stable consortia, synthesize not one but a whole range of enzymes capable of catalyzing not one but several biochemical processes associated with the destruction of organic pollutants.

Whole cells provide stabilization of the enzymatic NCs contained in them. This provides such complex microbial BCs with a number of advantages over free forms of enzymes—in particular, a longer period of semi-inactivation due to increased resistance to negative environmental factors [70].

In addition to the synthesis and storage of enzymatic NCs, whole microbial cells in the processes of pollutant destruction perform a number of auxiliary functions that contribute to increasing the efficiency of the process as a whole: the entire microbial biomass is a sorbent of hydrocarbon pollutants, increasing the contact surface and the area for the manifestation of catalytic activity; bacteria and phototrophs synthesize exopolysaccharides, which act as sorbents of hydrocarbon pollutants and also contribute to the formation of stable microbial populations characterized by increased biocatalytic activity against various xenobiotics [71]; bacteria are known for their ability to produce biosurfactants that exhibit the properties of surfactants that contribute to the removal of oil pollution; and microalgae

carry out the process of transformation of CO_2 into O_2 as result of photosynthesis, which, in the case of the functioning of consortia of cells with different enzymes, makes it possible to maintain metabolic activity of aerobic cells of different microorganisms in an active state and stimulate the oxidative destruction of various pollutants [70].

Each of the types of microbial cells has its own characteristics, which must be taken into account in their practical application. In the case of complex contamination, such as those discussed in this review, it is advisable to use consortia-containing cells destructing various organic compounds and toxic products of their primary (mainly oxidized) conversion. A high efficiency of degradation of pollutants can be achieved due to bionanocatalysts (enzymes) synthesized by these cells.

Consortia isolated directly from soils or effluents contaminated with petroleum hydrocarbons, as a rule, already contain the entire necessary list of producers because of the gradual formation of the microbiome necessary in composition due to the adaptation of microbial cells to pollutants present in their environment [46–49]. As a rule, such consortia are in a stabilized state due to self-immobilization on solid particles and with the participation of their own exopolysaccharides [70–72]. At the same time, such consortia may not have the highest target activity for the degradation of pollutants and require the presence of specific additives (co-substrates, growth inducers, synthesis of certain enzymes, etc.) in the case of their practical use (Figure 2).

An effective alternative in this case is synthetic (artificially created) consortia of microorganisms, which are deprived of a number of disadvantages of natural consortia due to the directed combination of highly active cells destructing toxicants and organic pollutants. When combining cells into consortia, individual characteristics of cultures and the possibilities of their combination are usually taken into account. It has been shown that it is expedient to stabilize such artificial consortia by immobilization into chemically stable, non-toxic carrier matrices [69,73].

The most efficiently functioning aerobic BCs for the degradation of oil-containing pollutants include immobilized cells of hydrocarbon-oxidizing microorganisms [54–56,58,59] and synthetic and natural consortia [1,4,46–53]. There are also successful variants of combining physical–chemical oxidative treatment of purified media with the use of nanomaterials in membrane aerobic bioreactors containing simultaneously working microbial consortia [68].

Anaerobic biotechnology is also widely used for wastewater treatment with petroleum hydrocarbons and their derivatives [2,28,61,62,74]. The effectiveness of its implementation depends on the interaction between the cells of microorganisms in an anaerobic environment, where many pollutants are converted into biogas.

The properties of oil-containing wastewaters vary depending on the industry in which they are formed and significantly affect the composition of the microbiome in an anaerobic reactor [75].

New technologies of oxidative desulfurization of hydrocarbon raw materials using promising NCs represent a promising alternative to the traditional energy-intensive hydrodesulfurization [76,77]. The waste of the technology contains oxidized sulfur-containing organic compounds extracted by adsorption or extraction from crude or treated oil. It has been shown that as a result of anaerobic conversion using immobilized artificially formed consortia, these wastes with residual concentrations of oil and high sulfur content can be successfully transformed into biogas with a high methane content [61,62]. Interestingly, the consortia themselves can be used repeatedly, and their conversion activity can be restored through the reactivation procedure.

It is known that under aerobic conditions, the aromatic ring in PAHs molecules is destroyed by a reaction with O_2, which, in addition to the co-substrate, is an electron acceptor, and the process proceeds with the participation of enzymatic BCs (monooxygenases and dioxygenases). In the absence of O_2, the aromatic ring is destroyed by the action of reductases and other electron acceptors. The biodegradation process is usually

slowed down due to the cytotoxicity of hydrocarbons and their high concentrations due to unfavorable environmental conditions or the presence of metabolic restrictions [78–80].

The use of microbial fuel cells (MFCs) has been shown for wastewater treatment. Sodium benzoate (0.721 g/L) and conventional wastewater treatment plants provided an electrical voltage of 0.6–0.8 V and a decrease in COD by 50–89% when using an artificial microbial consortium consisting of four bacterial strains [81]. Twenty MFCs based on the developed consortium, when connected to electrical series–parallel connections, were able to generate 2.3 V and a current of 0.5 mA. The potential for possible further applications of these hybrid MFCs-based systems for the decomposition of complex organic pollutants present in industrial wastewaters has been demonstrated [81].

Using MFCs, the possibility of oil wastewater treatment with simultaneous generation of electricity and COD decrease was investigated. Through oxidation in the MFCs systems with activated sludge, bioelectricity was generated and used in the cathode chamber [82]. The petrochemical wastewater from an acrylic acid planet with a high COD value has been investigated as a substrate for generating electricity in a dual-chamber of MFC with anaerobic sludge as a sample of BCs [83].

Despite the seemingly great prospects of MFCs, the expediency of their industrial implementation in the purification processes of petrochemical wastewaters remains a big question due to the difficulties with the organization of economically justified technical design of such processes. So far, the use of MFCs as parts of hybrid processes related to solving problems in the pharmaceutical industry looks the most realistic [84].

It should be noted that not only microbial cells with a large set of enzymatic activities are considered as BCs but also individual enzymes, although they are rarely found as components of well-known industrial purification technologies. Enzymes are proposed for use in the hydrolysis of polyacrylamide in the composition of petrochemical wastewaters [85]. An enzyme such as laccase was covalently immobilized on NPs of amino-terminated silanized magnetite. The use of the obtained bionanocomposites (bioNComs = "laccase-magnetite") enabled the treatment of artificial and real wastewaters with the extraction of the dye Eriochrome Black T and phenol. Optimal catalytic characteristics were achieved in the media with pH 4–4.5 [86]. Only laccase and other oxidoreductases (tyrosinase and horseradish peroxidase) were considered for phenol degradation [87]. It is more expedient to consider the use of enzymes in the immobilized form [88], including as a component of bioNComs [86].

The combined use of BCs and NPs provides an increase in the efficiency of the processes of purification of various natural objects and wastewater from hydrogen pollution; therefore, it seems promising from the point of view of further improvement of purification processes. A bioNCom such as Fe_3O_4-NIL-DAS@lac, which is a laccase immobilized on magnetic NPs modified by amino-functionalized ionic liquid using di-aldehyde starch (DAS) as cross-linker (Fe_3O_4-NIL-DAS), was used to extract phenol and its derivatives from wastewater. The maximum removal efficiency was 86.1%, 93.6% and 100% for phenol, 4-chlorophenol and 2,4-dichlorophenol, respectively [69].

The addition of graphene oxide quantum dots (GOQDs) to the reaction medium with *Bacillus cereus* cells caused the activation of cytokinesis and increased secretion of extracellular polymer compounds important for biofilm formation. As a result, an increase in the efficiency of decomposition of anthracene and phenanthrene was noted [67].

The combination of *Brevibacillus parabrev* cells with Fe_3O_4 magnetic nanoparticles contributed to an increase in the efficiency of tetradecane destruction due to Pickering emulsification and increased activity from BCs [64].

Chemically modified mesoporous silica NPs (mSNPs) (10 nm) were obtained, which represented a closed system with C_{18}-hydrocarbon chains in a closed collapsed state in an aqueous medium that is capable of opening due to solvation by lipophilic alkanes and releasing its contents upon contact with the oil phase. NPs have been successfully tested for the delivery of additional nutrients to BCs during the biodegradation of crude oil with *Marinobacter hydrocarbonoclasticus* [66].

The effect of the hybrid synergistic interaction of NPs of magnetite covered by polyvinylpyrrolidone (PVP)-coated iron oxide and oil-degrading bacterial cells was established [65]. At relatively high concentrations of crude oil (375 mg/L), due to rapid saturation only with magnetic NPs (MNPs), approximately 70% of alkane molecules with a carbon chain length of C_9–C_{22} and 65% of alkanes with a chain length of C_{23}–C_{26} can be removed in 1 h. Microbial bioremediation only after 24–48 h provided removal of 80–90% of oil, whereas a combination of MNPs with BCs such as *Halamonas* sp., *V. gazogenes* or *M. hydrocarbonoclasticus* cells provided 100% oil destruction for the same period of time. A similar effect was obtained during the degradation of naphthalene [63]. The successful decomposition of naphthalene was demonstrated with a combination of *S. aestuarii* 357 bacteria and functionalized MNPs such as FeNP-NDI-DA, obtained on the basis of Fe_3O_4 and the diimide-dopamine ligands. MNPs in an environment with naphthalene formed magnetic complex naphthalene@FeNP-NDI-DA during 0.5 h of stirring.

MNPs with different compositions and unique structural, chemical and functional characteristics were recommended for use in the demulsification and pretreatment of oil–water emulsions. It has been shown that different methods can be used to obtain MNPs: the hydrothermal method, co-precipitation, sol-gel synthesis, and synthesis with the use of redox reactions or microemulsification [89]. The most highly effective demulsifiers are obtained by modifying and functionalizing the MNPs surface, while it is important that the MNPs surfaces contain suitable polymers or surfactants [89].

Sponges modified with MNPs can repel water and selectively absorb organic solvents as well as various lubricating oils with high adsorption capacity from water. Two-stage fabrication of Fe_3O_4 polyurethane with polystyrene resulted in the production of a superhydrophobic magnetic sponge of PU@Fe_3O_4@PS. To obtain this hydrophobic, magnetic nanomaterial, photopolymerization was carried out under ultrasonic dip coating. A magnetic sponge was used for the effective remediation of oil and various organic solvents from water [90].

A wide range of different magnetic composite amphiphilic, hydrophobic and hydrophilic exterior/hydrophobic interior nanomaterials for demulsification and adsorption with the possibility of their reuse is known today: Fe_3O_4@oleic acid@graphene oxide, Fe_3O_4/ethyl cellulose, PU@Fe_3O_4@PS, PVP-coated iron oxide and polystyrene/Fe_3O_4/graphene aerogel [65,89,91–93]. It is obvious that further increasing the diversity among such developments will contribute to improving their characteristics and increasing their attractiveness for practical use.

4. Combined Applications of NCs and BCs for Elimination of Hydrocarbon Pollutants

It is known today that chemical-only or biocatalytic-only approaches are rarely used for deep wastewater treatment containing hydrocarbon pollutants. The mechanisms of action of NCs and BCs for individual application are described in detail in many articles and mainly depend on the chemical composition of hydrocarbon pollutants and catalysts, as well as the conditions for the treatment of contaminants [4,9,15,20,25,48,67]. The possibility of their combination at the secondary and tertiary stages of wastewater treatment is most often considered [10,94]. The development and implementation of NCs and NComs (Table 1) in combination with highly efficient BCs (Table 2) is the basis for successfully solving urgent problems related to the processes of water and soil purification from hydrocarbon pollutants. Two approaches to the integration of chemical and biocatalytic stages of wastewater treatment are known: (a) sequential physical–chemical and biocatalytic treatment conducted in different combinations and (b) the simultaneous carrying out of physical–chemical treatments and biodegradation in one reactor.

To choose a hybrid approach to the removal of pollutants, one of the key parameters is the initial chemical content of the cleaning object and the initial concentration of toxic components. At high concentrations of phenol in effluents, it is recommended to carry out preliminary chemical treatment in combination with further biocatalytic stages [95].

Petroleum refinery wastewater is a complex mixture of hydrocarbons, sulfides, ammonia, oils, suspended and dissolved solids and heavy metals. Depending on the type of wastewater (desalinated, acidic, spent alkaline and oily wastewaters), various sequential combined physical–chemical-biocatalytic purification methods are proposed at the secondary treatment stage (ozonation with treatment in a biofilm reactor with a movable layer or photocatalysis with treatment in a biofilm reactor with a compacted layer, etc.) [94,96].

For the purification of oilfield-produced water containing a mixture of suspended substances (including PAHs: pyrene, phenanthrene, anthracene and naphthalene) and dissolved organic (a mixture of phenol, benzene, xylenes, toluene and ethylbenzene) and non-organic (cations of barium, calcium, magnesium, sodium, potassium and heavy metals and anions such as chloride) compounds, biocatalytic treatment is usually carried out at the secondary stage of purification. Aerobic biocatalytic treatment is followed by a tertiary deep purification stage, which includes one or more stages: electrodialysis, macroporous polymer extraction (MPPE), microporous membrane treatment, electrolysis, ion exchange and AOPs [10]. In general, with the subsequent combination of several approaches to purification, the biocatalytic stages are now successfully combined with membrane technology, advanced oxidation processes (AOPs), electrochemical methods and other modern purification technologies. Among the advantages of hybrid sequential or one-time implemented processes, their environmental friendliness and the possibility of saving resources are indicated. Thus, for the complete mineralization of organic compounds, photocatalysis usually requires too much energetic costs and is often accompanied by the formation of dangerous by-products. The combination of photocatalysis and biodegradation joins the advantages of both technologies; is characterized by simple functioning, low energy consumption and high cleaning efficiency; and represents an actual direction of the current trend of research [97,98].

Membrane bioreactors are increasingly being offered as the technological design of hybrid processes associated with the deep purification of real wastewater [68,99]. Among the main competitive advantages of membrane technologies, it is possible to note the production of highly purified wastewater and the possible separation of growing biomass in a membrane bioreactor. In membrane bioreactors, biological purification is successfully combined with the microfiltration/ultrafiltration/nanofiltration/direct osmosis of effluents. At the tertiary stage of purification, membrane bioreactors are combined with membrane distillation and electrodialysis [100]. To improve the operation of membrane bioreactors, the use of various nanomaterials is being actively mastered [101]. Membrane systems based on nanomaterials provide an increase in the available flow rate per square unit of the membrane and contribute to the even more efficient removal of target contaminants with a longer period of membrane operation [100]. It is obvious that the development of membrane technologies in combination with nanomaterials with NCs and BCs is a fundamental trend in the current development of technologies for the elimination of hydrocarbon pollutants.

The successful application of a membrane bioreactor was demonstrated during the purification of petroleum refinery wastewater using a hybrid approach combining the intimate coupling of photocatalysis and biodegradation (ICPB) [99]. ICPB assumes the simultaneous carrying out of physical–chemical treatment and biodegradation in one reactor and ensures the achievement of good results in the decomposition of PAHs [97].

When combining different processes in one reactor, biodegradable intermediate products obtained as a result of the physical–chemical treatment of waste are immediately biodegradable. Thus, during the photocatalytic destruction of toluene, its partial transformation to biodegradable intermediates was ensured. Then, the appeared product was immediately mineralized by microorganisms [102].

Today, hybrid processes such as ICPB are known for the degradation of hydrocarbon pollutants (Table 3) [99,102–110] and some persistent and toxic organic pollutants [97]. At the same time, it can be argued that research in this direction is currently almost at the initial stage of development but will actively advance in the near future.

Table 3. Variants of the intimate coupling of photocatalysis and biodegradation (ICPB) for hydrocarbon pollutants treatment *.

Pollutants [Reference]	NCs/NCs; Size (nm) Physical or/and Chemical Treatment	BC/Co-Substrate	Removal Efficiency (%)
Naphthalene, Phenanthrene, Anthracene, Fluoranthene, Pyrene (PAHs) in soil (200 mg/kg) [103]	Ag_3PO_4@Fe_3O_4 UV-visible light photocatalyst (100–300 nm)	Adapted consortium (sewage sludge) in microcapsules of Ca-alginate gel and carboxymethyl cellulose	94% of PAHs mixture, ~100% of naphthalene, phenanthrene, anthracene, ~93% of fluoranthene, pyrene for 30 days
Phenanthrene in water (PAH) [104]	Composite Mn_3O_4/MnO_2-Ag_3PO_4 photocatalyst under visible light illumination	Biofilms with *Shewanella*, *Sedimentibacter*, *Comamonas*, *Acinetobacter* and *Pseudomonas*cells	96.2% degradation for 20 min, 100% non-toxic intermediates for 10 h
Phenanthrene in water [105]	Cu/N-codoped TiO_2 photocatalyst under UV or visible light illumination	PAH-degrading bacterial consortium with *Pseudomonadaceae* cells	UV (88.63% ± 0.71%) or visible light (62.87% ± 2.19%) from 10 mg/L for 6 h at room temperature; 9.31% ± 0.82% when only cells as BCs are used
Pyrene (PAH) [106]	Cu/N-codoped TiO_2 photocatalyst under visible or UV light illumination	PAH-degrading bacterial consortium	63.89% ± 1.03% (Visual light biol. treatment) >61.27% ± 1.08% (UV biol. treatment) >59.58% ± 1.15% (UV) >57.41% ± 1.13% (Visual light) >6.65% ± 0.72% (biol. treatment) >1.70% ± 0.34% (control)
Phenol, 4-chlorophenol (4-CP), and 4-fluorophenol (4-FP) [107]	N-doped TiO_2 (30 nm) coated POHFs/combined UV and visible light	Microbial consortium: *Scenedesmus obliquus* (*S. obliquus*) biofilm with *Rhodococcus* and *Pseudomonas* cells	The removals of DOC and COD of the phenolic compounds in mixture (1.06 mM phenol, 0.39 mM of 4-CP and 0.45 mM of 4-FP) for 11 h are ~98% and ~91%, respectively
Toluene [102]	N-doped TiO_2/PP	Microbial consortium	99%, with the elimination capacity of 550 g/m^3/h
1,2,4 trichlorobenzene [108]	Sugarcane cellulose-TiO_2	Microbial consortium	68.01%, which is 14.81% higher than that of biodegradation or photocatalysis alone, and the mineralization rate is 50.30%, which is 11.50% higher than that of photocatalysis alone
Phenol (100 mg/L) [109]	CdS@SiO_2@TRP nanocomposite photocatalyst under intermittent visible light irradiation	Adapted Pseudomonas putida cells	Simultaneous removal 97.24% of phenol for 10 h
Petroleum refinery wastewater [99]	Anatase nanocrystalline particles TiO_2 (14 nm), catalyst concentration	Microbial consortium in Membrane Bioreactor, pH 10	100 mg/L of TiO_2, 32% and 67% of TOC and TN for 90 min
Benzene (100 mg/L), toluene(100 mg/L), and xylene (100 mg/L) [110]	Zinc sulfide (ZnS) nanoparticles (20–90 nm), UV-A light, 28 °C, pH 4	*Aspergillus niger*	100% for 1 h

* TOC—total organic carbon; TN—total nitrogen; TRP—thermal-responsive polymer, which was composed of *N*-isopropyl acrylamide, acrylamide and the cross-linker *N*,*N*′-methylenebisacrylamide; PP—polypropylene; POHFs—photocatalytic optical hollow fibers; DOC—dissolved organic carbon.

Among the known ICPB processes involving NCs, processes with TiO_2 and its derivatives predominate, which provide the destruction of toluene [102], phenanthrene [105], pyrene [106], phenol, 4-chlorophenol (4-CP) and 4-fluorophenol (4-FP) [107], 1,2,4-trichlorobenzene [108] and petroleum refinery wastewater [99].

For those processes, where a comparative assessment of the effectiveness of joint and separate applications of biocatalysis and photocatalysis was carried out, the ICPB priority was shown [106,108]. The processes of hybrid biological and photocatalytic degradation of PAHs in soil with Ag_3PO_4@Fe_3O_4 and in water with Mn_3O_4/MnO_2- Ag_3PO_4 have been studied with the combined use of microbial BCs and NCs with photocatalytic activity in visible light [103,104]. The test of biocompatibility showed that Ag_3PO_4@Fe_3O_4 had practically no negative effect on the activity of soil microorganisms. These results open up new prospects for the joint use of photochemistry and biocatalytic technologies to solve urgent problems of environmental biotechnology, particularly for the removal of hydrocarbon pollutants.

For hybrid systems involving the combined use of chemical and biological catalysis, it is important to not only ensure the biocompatibility of components but also protect the activity of BCs. A hybrid photo-controlled reversible photocatalytic ICPB system has been developed with a mechanism of protecting microorganisms from the attack of reactive oxidative species formed during photocatalysis [109]. The surface of the CdS-photocatalyst was coated with SiO_2, and then a thermosensitive polymer (TRP) was applied to cover the surface of CDs@SiO_2. This polymer was composed of *N*-isopropyl acrylamide, acrylamide, and the cross-linker (*N*,*N*′-methylenebisacrylamide). The resulting CdS@SiO_2@TRP was attached to the surface of graphene (photothermal converter) to form a photo-controlled reversible photocatalytic system. Without light irradiation, soluble pollutants were biodegraded or absorbed by the CdS@SiO_2@TRP. Under light irradiation, reactive oxidative species, photogenerated due to the activation of the protective polymer cover, were formed inside CDs@SiO_2@TRP and photocatalytically decomposed the pollutants without contact between reactive oxidative species and microorganisms.

It should be noted that in hybrid systems, in addition to chemical and biocatalytic components, there is most often an important component such as a carrier, whose role is not limited to protecting BCs from the influence of negative environmental factors, particularly free radicals [111]. Among carriers, priority is given to biocompatible materials (cellulose, ceramics and loofah) [98,112]. Microcapsules based on Ca-alginate gel and carboxymethyl cellulose successfully protected BCs from direct contact with the photocatalyst and free radicals, increasing the life of BCs during the photocatalytic decomposition of PAHs [103]. Cellulose used as a carrier provided conditions for the growth of cells of the genus *Ruminiclostridium* used as BCs and played an additional role of co-substrate [108]. In this case, the cellulose carrier was not only biocompatible but also biodegradable. The presence of a co-substrate or its formation in the workflow can contribute to improving the efficiency of the implementation of hybrid processes. Not only the carrier but also low-molecular-weight substances (acetic or propionic acids formed in the bioreactor or introduced from outside) can also act as co-substrates and electron donors and contribute to the course of photocatalytic reactions [108]. Today, the development of hybrid processes depends on the development of three-dimensional carriers characterized as affordable, high strength, biocompatible, porous and reproducible in characteristics.

It should be noted that the effective use of hybrid processes is influenced by temperature and pH. Currently, a significant part of chemical reactions occurring in the presence of NCs do not require the use of extreme temperatures (Table 1), and this allows them to be considered in combination with BCs (Tables 2 and 3).

The use of sewage with natural microbial consortia, possessing activity at pH 5.5–7.4 (Table 2), can be considered optimal for simultaneous physical–chemical treatment and biodegradation, which generally corresponds to most modern approaches to the degradation of hydrocarbon pollutants using NCs (Table 1). If necessary, the range of operating pH values can be expanded when using microscopic fungi as BCs [110] and synthetic or adapted

consortia [46]. Thus, the use of *Aspergillus niger* cells in combination with NPs of ZS provides 100% destruction of 100 mg/L venzene, 100 mg/L toluene and 100 mg/L xylene w for 1 h at pH 4 [110]. BCs themselves play an important role in achieving the effective destruction of toxicants in the organization and implementation of hybrid processes [113]. It is possible to increase the activity of BCs by combining different cells and enzymes instead of their individual use [98]. This can also help to increase the stability of their action in the extended pH range. The selection of the BCs most suitable for combination, based on a deep knowledge of their properties, certainly underlies the further development of hybrid systems for purification from hydrocarbon pollutants.

5. Conclusions

Oil-polluted wastes and wastewaters represent the media with complex chemical compositions containing various components of hydrocarbon pollutants (PAHs, phenols, etc.). For the most effective destruction of them, the use of combinations of different physical, chemical and biological methods seems appropriate today. The fundamental trend in the development of technologies for the elimination of hydrocarbon pollutants is associated with the combined and synergistic application of membrane processes, various NCs, catalytic NComs and BCs. The main directions of the development of chemical degradation of hydrocarbon pollutants with the use of NCs and catalytic NComs are associated with advanced oxidation processes. The success of the implementation of aerobic and anaerobic biocatalytic processes is determined by the composition of microbial consortia possessing certain enzymatic activities. Their stabilization for application with some chemical NCs and their introduction into NComs give effective solutions in hybrid cleaning processes. The possibility of repeated use of heterogeneous biological and chemical catalysts should be noted among attractive characteristics of such catalytic combinations in addition to their high efficiency of action.

The information emphasized in this review is of practical importance for researchers who have interests in the area of development of new effective approaches to the elimination of hydrocarbon pollutants in accordance with strict environmental regulations. In addition, the discussed results disclose real promising directions in the development of all kinds of practically significant hybrid physical–chemical–biological processes characterized by high efficiency and reduced environmental load. In the purification processes of oil-polluted wastewaters, the combination of chemical and biological catalysts looks the most appropriate and successful for implementation at the stages of secondary and tertiary treatment of contaminated wastewater. To choose the best approach to cleaning based on NCs and BCs, the key parameters (the initial chemical composition of the cleaning objects and the initial concentration of pollutants) should be taken into account.

It is obvious that the existing oil-polluted wastewater treatment systems require urgent and significant modernization, since individual components of these pollutants are already detected even in specially protected environmental areas [114]. The severity of the problem is emphasized by the fact that wastewater, in addition to oily components, may contain difficult-to-degrade and difficult-to-separate microplastics [115], orbing all kinds of pollutants of different chemical natures, such as pharmaceutical pollutants [84], perfluorocarbons [72], organophosphorus compounds and, of course, various petroleum hydrocarbons [116–118]. This is a real way for the entrance of residual oil pollution (in a sorbed form on microplastic particles) into various aquatic ecosystems. The active involvement of new chemical and biological nanomaterials and NCs from other fields of application in purification systems can open up the simultaneous complex decomposition of organic pollutants and promising prospects for solving the above tasks.

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