



Review

Nanocatalysts for Oxidative Desulfurization of Liquid Fuel: Modern Solutions and the Perspectives of Application in Hybrid Chemical-Biocatalytic Processes

Olga Maslova ¹ , Olga Senko ^{1,2}, Argam Akopyan ¹, Sergey Lysenko ¹, Alexander Anisimov ^{1,2} and Elena Efremenko ^{1,2,*} 

- ¹ Faculty of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia; olga.maslova.rabota@gmail.com (O.M.); senkoov@gmail.com (O.S.); arvchem@yandex.ru (A.A.); ls@oil.chem.msu.ru (S.L.); sulfur45@mail.ru (A.A.)
² Emanuel Institute of Biochemical Physics, Russian Academy of Science, 119334 Moscow, Russia
 * Correspondence: elena_efremenko@list.ru; Tel.: +7-495-939-3170; Fax: +7-495-939-5417

Abstract: In this paper, the current advantages and disadvantages of using metal-containing nanocatalysts (NCs) for deep chemical oxidative desulfurization (ODS) of liquid fuels are reviewed. A similar analysis is performed for the oxidative biodesulfurization of oil along the 4S-pathway, catalyzed by various aerobic bacterial cells of microorganisms. The preferences of using NCs for the oxidation of organic sulfur-containing compounds in various oil fractions seem obvious. The text discusses the development of new chemical and biocatalytic approaches to ODS, including the use of both heterogeneous NCs and anaerobic microbial biocatalysts that catalyze the reduction of chemically oxidized sulfur-containing compounds in the framework of methanogenesis. The addition of anaerobic biocatalytic stages to the ODS of liquid fuel based on NCs leads to the emergence of hybrid technologies that improve both the environmental characteristics and the economic efficiency of the overall process. The bioconversion of sulfur-containing extracts from fuels with accompanying hydrocarbon residues into biogas containing valuable components for the implementation of C-1 green chemistry processes, such as CH₄, CO₂, or H₂, looks attractive for the implementation of such a hybrid process.

Keywords: oxidative desulfurization; nanocatalysts; immobilized biocatalysts; hybrid techniques; biotransformation of sulfones



Citation: Maslova, O.; Senko, O.; Akopyan, A.; Lysenko, S.; Anisimov, A.; Efremenko, E. Nanocatalysts for Oxidative Desulfurization of Liquid Fuel: Modern Solutions and the Perspectives of Application in Hybrid Chemical-Biocatalytic Processes. *Catalysts* **2021**, *11*, 1131. <https://doi.org/10.3390/catal11091131>

Academic Editor: Jose M. Palomo

Received: 1 September 2021

Accepted: 18 September 2021

Published: 21 September 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Petroleum and its fractions are currently the primary sources of energy (comprising ~50% the total global demand) and of raw materials for the chemical industry [1,2]. Sulfur is the most common heteroatom in raw oils, which tends to inhibit the activity of catalysts used in secondary oil processing [3]. Sulfur can be found in crude oil both in its pure form and in complex substances including mercaptans, sulfides, disulfides, and heterocyclic compounds such as thiophene (TH), benzothiophene (BT), dibenzothiophene (DBT), condensed polynuclear aromatic hydrocarbons and its derivatives. The total number of various sulfur-containing organic compounds found in petroleum is more than 200 [4–6]. Burning of sulfur-containing fuel causes emission of sulfur oxides (SO_x), therefore the presence of sulfur in fuel has a negative environmental impact.

These gases react with water in the atmosphere to form sulfates and acid rain which damage buildings, acidify soil, and ultimately lead to deforestation, as well as degradation of various other ecosystems [7,8]. The increasingly strict international environmental standards on SO_x emission control lead to the growing demand for petroleum and refined products with ultra-low sulfur content, namely, below 5–10 ppm [5,9].

The industrially realized the oxidation demercaptanization technique in the presence of an alkaline solution ensures efficient removal of sulfur-containing mercaptans from

dry and liquefied hydrocarbon gases, gasoline fractions, light oils, and gas condensates. The demercaptanization processes include such techniques as Merox, Merikat, Demerus, and Demercaptanization of Distillate. These approaches allow reducing the total sulfur concentration to 10 ppm in the propane-propylene fractions, butane-butylene fractions, and their mixtures containing mainly methyl- and ethyl mercaptans. The many advantages of oxidation demercaptanization technique are however offset by its limited applicability in case of heavy and extra-heavy oils fractions [10–12].

Hydrodesulfurization (HDS) is another approach for removal of aliphatic and acyclic sulfur-containing compounds from liquid fuels, which is widely used on an industrial scale. However, HDS has a relatively low efficiency for the removal of polyaromatic sulfur-containing molecules such as BT, DBT, and their alkyl-substituted derivatives, e.g., 4,6-dimethyldibenzothiophene (4,6-DMDBT), due to steric hindrance. Reducing sulfur concentration to 10–50 ppm in the course of HDS requires increased consumption of hydrogen, realizing rather strict conditions (300–400 °C, 30–130 atm), and usage of complex equipment. All these factors result, as a rule, in deposition of coke on the catalyst's surface, reduction of the energy density of the resulting fuel, and high operating costs for the process [5,8,13–17].

Alternative desulfurization techniques can be applied for deeper desulfurization, either in addition to HDS or separately. These approaches include chemical oxidative desulfurization (ODS), oxidative biodesulfurization (OBDS), photooxidation, adsorption, extraction, etc. [2,6,9,18,19].

Among these, ODS is currently the most actively studied and applied one, because it can best meet the strict requirements of the modern environmental standards [3,20–22]. The ODS can ensure efficient treatment of the sulfur-containing oil with oxidants at low temperature, under ambient pressure, and with zero H₂ consumption. ODS can convert the sulfur-containing compounds to highly polar sulfoxides or sulfones, which can be subsequently removed from the purified oil fractions, e.g., with extraction or adsorption [23,24].

The really inviting perspectives for the practical implementation of ODS can be opened via development and application of new-generation heterogeneous nanocatalysts (NCs), including nanocomposites. Increased interest in modern NCs is predefined by high activity, selectivity, and stability of their action. For the effective implementation of ODS, it is required to minimize possible losses associated with non-selective oxidation of hydrocarbon components of fuels. Therefore, increased selectivity of the oxidation process is one of the most key objectives of the ODS, since it directly affects the cost of purification. NCs can be easily concentrated in the required locations of the reaction system, including phase interfaces, which provide the greater part of the relevant chemical reactions in the course of ODS [25]. The purified oil fractions can be easily separated from the NCs, and multiple re-use and regeneration of the NCs is most often quite feasible [16,26,27]. The most often suggested scenario permits preventing losses of hydrocarbon backbone in the course of ODS implies desulfonylation, i.e., cracking of the sulfone molecule directly in the fuel to produce volatile SO₂ and the hydrocarbon backbone. This can be implemented exactly via NCs based on oxides and hydroxides of alkaline and alkaline earth metals [28,29]. The selectivity of interaction between DBT and such nucleophiles as hydroxide ion in the course of desulfonylation is known to be enhanced via introduction of multiatomic organic alcohols such as ethylene- and propylene glycol into the reaction medium [29]. The adsorbents capable of capturing the SO₂ produced in the course of desulfonylation are usually chosen among the oxides of rare earth metals [30]. However, desulfonylation has several essential drawbacks. These include the relatively strict conditions (temperature higher than 270 °C, pressure higher than normal) required for the chemical reactions capable of destroying the oxidized sulfur-containing compounds for extracting SO₂. Moreover, these reactions sometimes have a low selectivity and fail to ensure the preservation of the hydrocarbon backbone in the treated oil fractions [29]. Therefore, researchers developing new ODS approaches currently prefer extraction as the technique for removing the oxidized forms of sulfur from the treated fuel.

The environment-friendly features of the emerging products and technologies in petrochemical and petroleum industries can be enhanced via introducing biocatalytic stages into the technological cycle. Application of microbial biocatalysts (BCs) was proven to be beneficial for biological treatment of petrochemical wastewater [31–34] and for oxidative biodesulfurization (OBDS) of petroleum via the 4S-pathway [6,35,36]. In the latter case the biocatalytic oxidation caused by the enzymes, which are produced by the bacterial cells, implies conversion of sulfur-containing organic compounds into the oxidized form, sulfone (e.g., DBT is converted into DBTO₂). This is followed by biotransformation of the sulfone, which occurs in several stages (Figure 1).

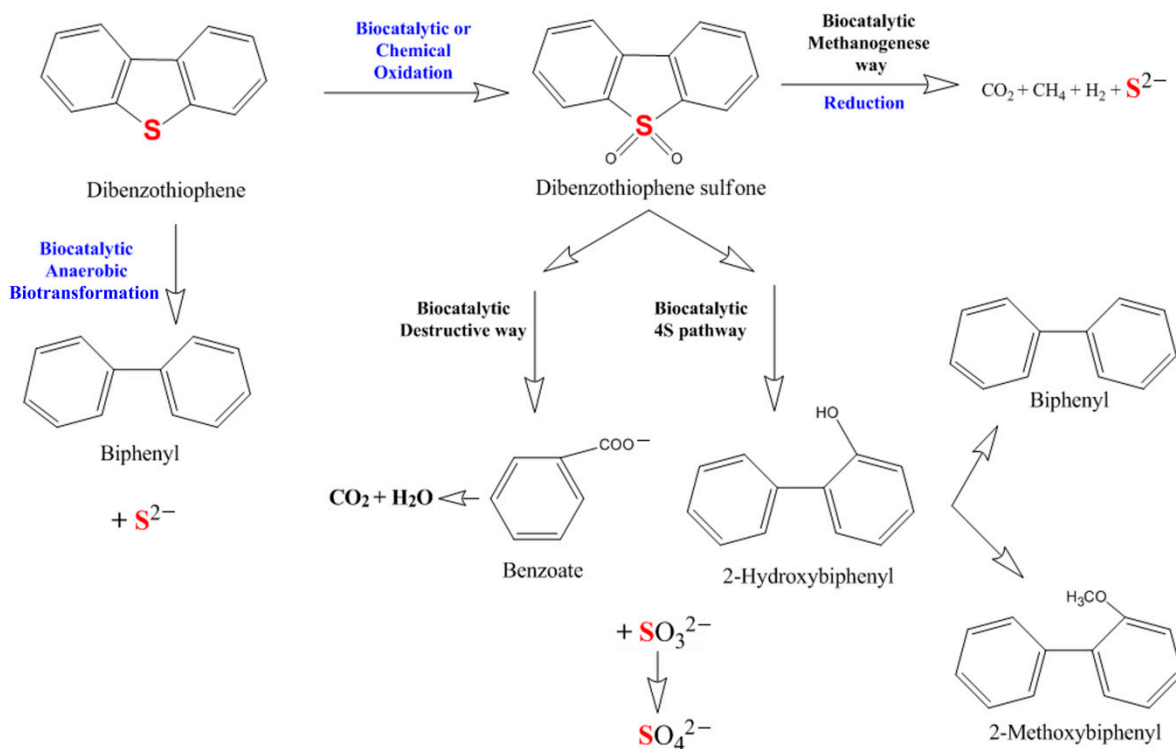


Figure 1. Possible pathways for transformation of DBT and its sulfone (DBTO₂) in the presence of BCs.

Other pathways for biotransformation of sulfones are also known, such as destructive way or methanogenesis. The 4S-pathway and the destructive way cause the sulfur to be extracted from the sulfone in the form sulfite and sulfate. Under anaerobic conditions the sulfur is extracted in the sulfide form, and this approach is known as anaerobic biotransformation or methanogenesis way). Thus, biodesulfurization (BDS) can lead to extraction of sulfur either in the oxidized or in the reduced form. Adding biocatalytic stages to ODS processes can both enhance the environment-friendly features of the new hybrid technologies and increase their economic attraction (Figure 1). For example, a deeper desulfurization of fuel after ODS (chemical oxidation and extraction) can be performed via oxidative 4S-pathway in the presence of microbial BCs. Moreover, the sulfur-containing extracts with residual hydrocarbons can be converted under the action of microbial BCs into biogas rich in such valuable components for C-1 chemistry as CH₄, CO₂, and H₂ [24].

This review is aimed at analysis and systematization of information accumulated up to date in the research fields described above. A special attention is paid to the successful solutions in creating NCs for ODS and achievements in developing essentially novel comprehensive hybrid biochemical approaches to oxidative desulfurization involving heterogeneous chemical NCs and microbial BCs, which comply with the basic principles of green chemistry.

2. Components for the Formation of Nanostructured Catalysts, Oxidants, and Extractants for Oxidative Desulfurization of Liquid Fuels

Known ODS processes in liquid fuels are performed in liquid or gas–liquid media. ODS in a gas–liquid media occurs in the presence of heterogeneous catalysts such as $\text{MnO}_2/\text{Al}_2\text{O}_3$ and $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ at relatively high temperatures (130–200 °C) and pressure (10 bar), with ozone, nitrogen oxide (IV), or oxygen used as oxidants. Such processes have relatively low selectivity towards sulfur atoms [37]. Therefore, ODS in liquid media is currently preferred due to energy efficiency considerations.

The following substances were tested as oxidants for ODS in liquid media: sulfuric acid, nitric acid, potassium permanganate, sodium bromate, potassium persulfate, hypochlorites, carboxylic and sulfonic peracids, tert-butyl hydroperoxide (t-BuOOH), tert-amyl hydroperoxide, etc., as well as hydrogen peroxide (H_2O_2), pure or in combination with short-chain organic acids, etc. [17,25,38–41]. Many of these substances were found to be inefficient, mainly due to the limitations connected with low selectivity, low end product output, high cost, toxicity, etc. Among these approaches, involving H_2SO_4 appeared to be best suited for industrial-scale application; however, even this way was discounted as impractical due to environmental implications, in particular, formation of large quantities of resins and acidic refuse.

In view of the abovementioned factors, many researchers nowadays prefer liquid peroxide oxidants, in particular, hydrogen peroxide, due to its availability and environment-friendly properties. The sole product of H_2O_2 reduction is water. H_2O_2 was shown to be efficient as oxidant of TH, BT, DBT, and their alkyl derivatives. H_2O_2 was mentioned as one of the basic substances in one of the three key approaches to the development of green chemistry [42].

It was shown that to enhance the activity of the oxidants in the ODS processes, these substances should be used in combination with organic or inorganic acids such as formic acid, acetic acid (CH_3COOH), oxalic acid, benzoic acid, H_2SO_4 , and carbonic acid. It was established that the oxidation reactivity of inorganic acids is lower than that of organic acids [23]. The highest oxidative activity is shown by organic peracids which are formed in situ via interaction of H_2O_2 with such available short-chain carboxylic acids as formic acid and acetic acid.

One of the drawbacks of using H_2O_2 as oxidant is the formation of water in the reaction medium which makes the system a two-phase one and therefore limits the mass transfer. Additionally, part of the fuel gets into the extract in the course of separation of the liquid phase. This problem can be solved by using peroxide oxidants soluble in the fuel [43]. The hydroperoxides of tert-amyl, tert-butyl, and cumene in the presence of lower carboxylic acids ensure the formation of oxidized forms of sulfur-containing compounds from the oil fractions with output of up to 94% [44]. However, the high cost of such oxidants limits the perspective of their industrial application.

Development of NCs in the form of nanocomposites allows increasing the oxidative activity of the reagents, enhancing the desulfurization efficiency, and extending the application range for H_2O_2 in ODS (Tables 1 and 2). Additionally, subjecting the resulting sulfur-containing extracts with residual hydrocarbon content to resource-saving biocatalytic technologies allows minimizing the losses of hydrocarbon backbone during ODS, reducing the quantity of waste, and enhancing the overall environmental friendliness of the desulfurization technology [24,45–47].

Table 1. Examples of NCs for ODS of gasoline with initial sulfur concentration 398–500 ppm.

NCs	NC Size (nm)	Conditions of ODS	ODS Efficiency (%)	Ref.
(C ₄ H ₉) ₄ N) ₆ Mo ₇ O ₂₄ /PVA ¹	67	40 °C, 2 h, 500 rpm, H ₂ O ₂ /CH ₃ COOH, * mr = 1	97.0	[19]
K ₅ PMo ₁₁ CuO ₃₉ -MgCu ₂ O ₄ @PVA	35–38	35 °C, 1 h, 600 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 1	97.6	[16]
PMnW ₁₁ /mGO ²	45	35 °C, 1 h, H ₂ O ₂ /CH ₃ COOH, mr = 2	97.2	[48]
CTAB ³ -PTA ⁴ /CS ⁵	36	35 °C, 1 h, 500 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	94.9	[49]
FeW ₁₁ V/CTAB-MMT ⁶	50	35 °C, 1 h, 700 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	96.6	[50]
IMID ⁷ /PMA/CS	65	35 °C, 1 h, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	96.4	[26]
Fe ₂ W ₁₈ Fe ₄ /NiO/CS	46.5	35 °C, 1 h, 700 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	97.1	[51]
PMnW ₁₁ /TiO ₂ /CS	21	30–35 °C, 1 h, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	97.0	[52]
TBA ⁸ -PV ₂ Mo ₁₀ /PVA	21	35 °C, 2 h, 500 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 1	97.0	[53]
Fe ₂ W ₁₈ Fe ₄ ⁹ /FeTiO ₃	40–50	35 °C, 1 h, 700 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	98.0	[54]
IMID-KTHPA ¹⁰ /CS	61	35 °C, 1 h, 500 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	97.0	[55]
TBA-Si ₂ W ₁₈ Cd ₄ /PVA	33	35 °C, 1 h, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	96.7	[23]
TBA-PWFe/NiO/BNT ¹¹	32	35 °C, 1 h, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	98.0	[56]
t-B.PWFe ¹² /NiO	10–100	35 °C, 1 h, 600 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	97.0	[57]
PMo ₁₂ O ₄₀ /MnFe ₂ O ₄₀ with <i>Aloe vera</i> leaf extract	70.5	35 °C, 1 h, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	98.0	[25]
TBA-SiWMn ¹³ /PVA	33	35 °C, 2 h, 1500 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	96.9	[8]
[(FeW ₉ O ₃₄) ₂ Fe ₄ (H ₂ O) ₂] ^{−10} (Fe ₆ W ₁₈ O ₇₀)	17	35 °C, 1 h, 500 rpm, H ₂ O ₂ /CH ₃ COOH, mr = 0.5	98.0	[58]

* mr—molar ratio; ¹ PVA—poly(vinyl alcohol); ² mGO—modified graphene oxide; ³ CTAB—cetyltrimethylammonium bromide; ⁴ PTA—phosphotungstic acid; ⁵ CS—chitosan; ⁶ CTAB-MMT—cetyltrimethylammonium bromide modified montmorillonite; ⁷ IMID—imidazolium C₃H₄N₂; ⁸ TBA—tetrabutylammonium bromide; ⁹ Fe₂W₁₈Fe₄—tetranuclear sandwich-type polyoxometalate (Na₉K[(FeW₉O₃₄)₂Fe₄(H₂O)₂]₃₂H₂O); ¹⁰ KTHPA—Keggin-type heteropolyanion [PW₁₂O₄₀]; ¹¹ BNT—sodium activated bentonite; ¹² t-B.PWFe—[n-C₄H₉]₄N₄H[PW₁₁FeO₃₉]; ¹³ TBA-SiWMn—Silicotungstate polyoxometalate ((n-C₄H₉)₄N)₇H₅Si₂W₁₈Mn₄O₆₈.

Modern NCs for ODS generally belong to metal oxides or metal-containing heteropolymeric compounds designated as polyoxometalates (POMs), or, more seldom, to other chemical compound types (molybdenum disulfide, etc.) or metals (Pd, Au, etc.).

The NCs are usually modified in order to stabilize them, to enhance their activity, to increase the catalyst/reagent contact surface, to impart the magnetic properties to the catalysts (in order to facilitate the extraction of the NCs from the reaction medium) (Tables 1 and 2). For known NCs based on metal oxides the ODS efficiency depends on the combination of NC/carrier/oxidant and decreases in the series: WO₃/few layer g-C₃N₄/H₂O₂ > α-Fe₂O₃/H₂O₂/glacial acetic acid > CoMo/rGO/H₂O₂ > MnO₂/tert-butyl hydroperoxide (TBHP) > MoO₃/Si/PVA/H₂O₂ (Tables 1 and 2) [7,20,43,59].

The main attention in developing novel catalysts for ODS reaction is nowadays paid to POMs, which are a unique class of negatively-charged metal-oxygen clusters with excellent catalytic properties [26]. Oxygen atoms in such compounds are usually present in the form of bridging- or end-oxo ligands. POMs have strong Bronsted acidity, are capable of multi-electron redox transformation under mild conditions, and have variable acid-base and redox properties. The main features of POMs include their thermal stability, superoxidative activity, and controllable redox potential [49]. The M and X atom in POMs appear in their highest level of oxidation state which makes them more reactive. The examples of such compounds are polyoxoanions with primary Keggin structure mono-substituted with a transition metal [XM₁₁TMO₃₉]^{n−}, where X = P, Si, B; M = W, Mo; TM = transition metal [27], negatively-charged polyoxoclusters with general formula [XM₁₂O₄₀]^{n−} (n = 3, 4)

which are composed of the addenda atoms M (M is an early high-valent d-block transition metal in a high oxidation state and typically = Mo^{IV} , W^{VI} , V^{V} , Nb, Ta, etc.) and the heteroatom X (central heteroatom X is often one of Al^{III} , Si^{IV} , or P^{V} , but can also be of another element such as Ge^{IV} , Fe^{III} , or Co^{II} , etc.), XO_4^{n-} tetrahedron unit via 12 octahedron MO_6^{n-} units, and also several Keggin derivatives can be formed by removing one or more MO_4^{4+} units [56,57,60,61], Dawson-type polyoxometalate $[\text{P}_2\text{W}_{18}\text{O}_{61}(\text{O}_2)]^{6-}$ [62], as well as Anderson-type polyoxometalate such as the $((\text{C}_4\text{H}_9)_4\text{N})_6\text{Mo}_7\text{O}_{24}$ [53]. The vanadium-substituted Keggin type polyoxometalate catalyst was found to be very active in ODS of gasoline [53]. Due to solubility of POMs in water and polar fractions, their application as homogeneous NCs and their separation from the reaction medium is limited. The POMs are also characterized by a relatively low surface area (1–10 m^2/g). Therefore, formation of heterogeneous NCs via immobilization of POMs on environment-friendly and available supports is suggested for efficient application of these catalysts in ODS (Table 1) [63].

In recent years many strategies have been developed to immobilize homogenous POMs in various supports to form new catalytically active and easily recoverable materials (Tables 1 and 2) [64]. NCs for ODS have been developed via deposition of POMs on mesoporous materials such as graphene oxide GO, as well as NiO, PbO, Al_2O_3 , ZrO_2 , TiO_2 , SiO_2 , and other oxides [2,13,27,49,51,52,65–68], ceramic materials (such as MgCu_2O_4 , MnFe_2O_4) [16,60], mesoporous mesostructured silicates (MCM-41, SBA-15, etc.) [69], natural microporous materials (such as zeolites, bentonites, montmorillonite (MMT), etc.), polymeric organic supports (poly(vinyl alcohol) (PVA), chitosan (CS), etc.), and metal-organic frameworks (MOFs) [64].

The attractive features of PbO as carrier particles are their oxidative properties, the simplicity of their preparation and regeneration [27]. The NiO particles are considered perspective due to the high specific surface, zero environmental toxicity, and availability; they are an inexpensive semiconductive material [51,56]. The advantages of TiO_2 are its non-toxicity, as well as high thermal and chemical stability [52].

Graphene oxide (GO) is chosen by researchers for use in NCs due to its chemical stability, electric conductivity, and large specific surface area [2,48].

Ceramic materials with structure AB_2O_4 , e.g., MgAl_2O_4 , and MgCr_2O_4 , were proven to be efficient catalysts for oxidation of hydrocarbons [70].

Table 2. Examples of NCs used for ODS of model oil and real liquid fuels.

Liquid Fuel	NC	NC Size (nm)	Conditions of ODS	* S_0 , ODS Efficiency	Ref.
Model oil with one sulfur containing compound	$\alpha\text{-Fe}_2\text{O}_3$	-	1 h, $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$	500 ppm, DBT 99.5%	[59]
	$\text{MoO}_3/\text{Si}/\text{PVA}$	48	60 °C, 2.5 h, H_2O_2	500 ppm, DBT ~93.7%	[71]
	CoMo/rGO	-	60 °C, 1 h, H_2O_2	500 ppm, DBT 99.0%	[72]
	$\text{WO}_3/\text{few layer g-C}_3\text{N}_4\text{-composite}$	-	50 °C, 1 h, 800 rpm, H_2O_2	500 ppm, 100%, the oxidative reactivity order DBT > 4-MDBT > 4,6-DMDBT > 3-MBT	[73]
	[Bmin 1] $_{3\text{PMo}_{12}\text{O}_{40}}/\text{g-C}_3\text{N}_4$	-	40 °C, 2 h, H_2O_2 , 250 W high-pressure sodium lamp	1000 ppm, DBT ~95.0%, 4,6-DMDBT ~85.0% or BT ~70.0%	[74]
	$\text{Mo}/\text{Al-SBA15}^2$	-	60 °C, 30 min, H_2O_2	500 ppm, the oxidative reactivity order 4-methyl phenyl sulfide = dibenzyl sulfide = DBT > 4,6-DMDBT > methylDBT > BT > 5-methylBT	[69]

Table 2. Cont.

Liquid Fuel	NC	NC Size (nm)	Conditions of ODS	* S ₀ , ODS Efficiency	Ref.
Model oil with mixture of sulfur containing compounds	PMo/HKUST-1 ³	-	65 °C, 2 h, H ₂ O ₂	500, 250 and 250 ppm, respectively, DBT—95.0%, methyl phenyl sulfide (MPS)—98.0% and TH—90.0%	[61]
	PW ₁₁ Zn ⁴ /MIL-101 ⁵	50–400	50 °C, 2–3 h, H ₂ O ₂	500 ppm, ~100% from of each, the oxidative reactivity order DBT > 4,6-DMDBT > BT	[64]
Gasoil	((n-C ₄ H ₉) ₄ N) ₄ [PW ₁₁ Fe(H ₂ O) ₃₉ /PbO	62	60 °C, 2 h, CH ₃ COOH/H ₂ O ₂	97.0%	[27]
	Ni/SiO ₂ /PWA ⁶	25–45	Microwave 400 W, 4 min, 70 °C, H ₂ O ₂	510 ppm, 92.1%	[65]
Crude oil	H ₅ PMo ₁₀ V ₂ O ₄₀ /Fe ₃ O ₄ /g-C ₃ N ₄	23	80 °C, 200 min, H ₂ O ₂	500 and 1,900 ppm, 24.3% and 29.8%, respectively	[75]
Gas condensate	2D-porous MoS ₂		75 °C, 2 h, 600 rpm, H ₂ O ₂	2,850 ppm, 93.4%	[76]
Commercial diesel fuel	MnO ₂ , nanoflowers	40	60 °C, 35 min, 900 rpm, t-BuOOH	550 ppm, 81.9%	[43]

* S₀—initial sulfur concentration, ¹ Bmin—1 -butyl-3-methylimidazole, ² SBA-15—Mesoporous Silica Molecular Sieve SBA-15, ³ PMo/HKUST-1—(Cu₃(1,3,5-benzenetricarboxylate)₂H₃PMo₁₂O₄₀), ⁴ PW₁₁Zn—(n-C₄H₉)₄N_{4.2}H_{0.8}[PW₁₁Zn(H₂O)₃₉]·5H₂O, ⁵ MIL-101—MOF based on polymeric terephthalate, ⁶ PWA—phosphotungstic acid.

Inorganic ceramic supports are also actively used in development of NCs for ODS due to their physicochemical characteristics, environmental friendliness, stability, safety and ease of production, and low cost. Such ceramic nanoparticles as MgCu₂O₄ [16], MnFe₂O₄ [60], FeTiO₃ [54], as well as CuFe₂O₄ [58], etc., were successfully used as matrices for NCs for ODS.

The advantages of mesoporous mesostructured silicates (MCM-41, SBA-15, etc.) as supports for the development of NCs include large surface area, large pore volume, and their ordered structure. Moreover, the internal pore surface of such substances has a high chemical activity, which can lead to the formation of covalently bound (grafted) monomolecular layer of a chemical modifier on this surface. This layer can increase the efficiency of the catalyst's attachment to the support [77]. In contrast to MCM-41, SBA-15 has a higher pore size and stronger pore walls, which explains the preference given to SBA-15 by many researchers when developing NCs [69,78].

A natural mineral montmorillonite (MMT), which is a complex of aluminium magnesium silicate clay materials with a well-developed layered structure, has also been tested as support for NCs for ODS [50]. The chemical and mechanical stability, non-toxicity, and availability of large natural deposits make MMT an ideal carrier for immobilization of POMs [50]. A similar material, bentonite, was also considered as a suitable support for development of NCs due to its high adsorption properties, low cost, ease of preparation, and thermal stability [56].

The following materials have also been suggested and successfully tested as supports for immobilization of POMs: natural biodegradable polysaccharide chitosan (CS, a linear polymer of 2-amino-2-deoxy-β-D-glucan), which has a high adhesive ability and chelating properties [26], as well as PVA, which is non-toxic, environment-friendly, water-soluble, biocompatible, stable towards acids, and has a low cost [16,19]. Formation of NCs using CS can be achieved due to the free amino- and hydroxy-groups of the carrier and the active groups of the POM. Hydroxy groups of PVA can be a source of hydrogen bonds, which facilitate the formation of composites based on this polymer [79]. Synthesis of hybrid composites based on PVA and nanoceramic materials (such as magnesium cuprate MgCu₂O₄) is considered as yet another perspective approach to development of NCs for ODS [16].

Extract of *aloe vera* was used as a reductive and stabilizing agent for the formation of NCs via sol-gel technique, which was found to be environment friendly and to have a

low cost. Application of the resulting NC with formula $\text{PMo}_{12}\text{O}_{40}@\text{MnFe}_2\text{O}_4$ ensured ODS efficiency of 98% at 35 °C [25].

Graphite carbon nitride ($\text{g-C}_3\text{N}_4$), the most stable allotrope of carbon nitrides, which is widely used for photocatalysis, was also studied as support for immobilization of POMs and metal oxides for the development of NCs. The advantages of this carrier are its high chemical and reasonable thermal stability, its two-dimensional layered structure, and high availability of precursors [73–75,80,81]. It can be synthesized using the thermal polymerization of melamine, dicyandiamide, urea, etc., in a one-step process.

Various MOFs were also considered as carriers of POMs for development of efficient heterogeneous NCs. MOFs have such advantages as large surface volume, open crystalline structure, regulated pore size, functionality, etc. MOFs' structure features large, regular, available cells and channels, which can act as nanoreactors, because they can contain catalytically active molecules. All these features make MOFs (HKUST-1, MIL-101, etc.) perspective as components of NCs [61,64].

Three hybrid composite NCs for ODS were prepared via inclusion of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo), and $\text{H}_3\text{SiW}_{12}\text{O}_{40}$ (SiW) into a porous organometallic HKUST-1 framework (also called MOF-199) with composition of $\text{Cu}_3(\text{BTC})_2$, where BTC is benzene-1,3,5-tricarboxylate [61]. The best results for desulfurization of model fuels were achieved with PMo@HKUST-1, which could also be used in batch mode.

3-D polymeric MOF MIL-101(Cr) was built of carboxylate trimers $\text{Cr}_3(\text{OOCR})_6$, joined with terephthalic acid anions thus forming a “supertetrahedron” [82]. The mesoporous framework of MIL-101(Cr) was found stable while heated up to 350–375 °C. In addition to the high thermal and chemical stability, this framework also has a high porosity, which is a useful feature for developing NCs. NC was formed by the incorporation of the zinc-substituted polyoxotungstate anion $[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}]_5^-$ (PW_{11}Zn), into MIL-101(Cr) nanocages ($\text{PW}_{11}\text{Zn}@\text{MIL-101}$). Upon the completion of the ODS process, the reaction system contained only 3 ppm of 4,6-DMDBT and 16 ppm of 1-BT [64].

Modification of POMs with quaternary ammonium salts $\text{NR}_4^+ \text{X}^-$ was found to be useful for preparing NCs with interphase mass transfer properties. Here, R is an alkyl or aryl group, and X is usually a halide ion. Lipophilic cation (NR_4^+) (such as tetrabutylammonium) in the POMs is an efficient interphase mass transfer agent, and transports the peroxometal anion in the NC into the hydrophobic organic phase of the medium subjected to desulfurization [53,56]. The oxidation reactivity of the POM-based NC depends on the type of the counteranion and decreases in the following series: $(\text{C}_4\text{H}_9)_4\text{N}^+ > \text{NH}_4^+ > \text{K}^+$ [23].

NCs are usually characterized by Fourier transform infrared spectroscopy (FTIR), ultraviolet–visible (UV–vis), X-ray diffraction (XRD), and scanning electron microscopy (SEM) techniques. The particle sizes calculated using the Debye–Scherrer formula from X-ray diffraction data for the abovementioned NCs are within the range of 17–400 nm (Tables 1 and 2). The calculated diameter of $\text{g-C}_3\text{N}_4$ -based NCs was ca. 20–25 nm. The calculated sizes of the NCs developed based on MOFs are greater than in case of other carriers, and can be as high as 50 nm or more.

According to the mechanisms of catalytic reactions suggested by the researchers, NCs most often act as oxygen transfer agents, are converted into peroxide particles, or facilitate dissociation of the oxidant, and ensure selective oxidation of sulfur-containing compounds [25,27,43,48,53,57,74–76,83–85]. It was shown using the examples of $4\text{PW}_{11}\text{Fe}@\text{PbO}$ nanocatalyst and $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ oxidant that the kinetics of sulfur oxidation in the course of ODS is of the pseudo first-order type [27].

According to the literature, the efficiency of the oxidative activity of the NCs depends on the amount of electron density of the sulfur atom and the spatial structure of the sulfur-containing compound [69]. The reactivity of substrates increases along with the electron density of the sulfur atom. It was established that when hydrogen peroxide and formic acid are used as oxidants, the derivatives of TH with relatively low electron density on sulfur atoms (5.696 to 5.716) are the hardest to oxidize. BTs with electron density of 5.739 are more prone to oxidation, as are BT- and DBT-derivatives with still

higher value of this parameter [86]. This trend was also found for other sulfur-containing compounds, so that the efficiency of the oxidant decreased in the following series: 4-methylthiophenol > 4-chloro thiophenol > *n*-butyl mercaptan [48]. The electron density on the sulfur atom is 5.758, 5.759, and 5.760 for DBT, 4-methylbenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT), respectively. The differences between these parameters are too low to have an essential impact on the ODS efficiency for these compounds. Therefore, the difference in the efficiency of the sulfur atom's oxidation in this case can be attributed to the spatial structure of the compounds containing methyl groups. The ODS efficiency of the WO₃/few layer g-C₃N₄ composite used as NC decreases in the series: DBT > 4-MDBT > 4,6-DMDBT. The 3-methylbenzothiophene (3-MBT) had the lowest desulfurization efficiency compared to DBT, 4-MDBT, and 4,6-DMDBT due to the lowest electron density of the sulfur atom (5.572) for this compound [73].

The efficiency of Mo/Al-SBA15 as an NC for ODS changed in the series starting with DBT and decreasing for the derivatives with lower electron density or greater steric hindrances: 4-methyl phenyl sulfide (MeSPh) > dibenzyl sulfide (Bn₂S) = DBT > 4,6-dimethylDBT (Me₂DBT) > methylDBT (MeDBT) > benzothiophene (BT) > 5-methylbenzothiophene (MeBT) [69]. The desulfurization efficiency of most of the known NCs for ODS was found to decrease in the series: DBT > BT > thiophene (TH) (Tables 1 and 2), whereas the trend for hydrodesulfurization (HDS) was exactly reversed: THs > BTs > DBTs [18]. Thus, modernization of the techniques for deep desulfurization can include a combination of ODS and HDS.

Nitrogen-containing compounds are known to have a negative effect on the ODS process. The reaction rate for the oxidation of DBT in the presence of these nitrogen-containing compounds decreased in the order: indole > quinoline > pyrrole > pyridine. These results suggest that the negative effect of nitrogen-containing compounds on the ODS process is due to the competition with the sulfides for adsorption on the catalytic sites, as well as their basic character. However, this negative effect is minimal [75].

Many of the modern NCs were successfully tested using real raw material, and not only model test media, which is important (Tables 1 and 2). According to the published data, the duration of the oxidation stage does not exceed 3–6 h, and is usually within the 10–60 min range [87–89]. The data for the following NCs and supports are summarized in Table 1: the combination of peracetic acid (acetic acid/hydrogen peroxide with mole ratio of 1:1 or 1:2) and the known NCs based on Anderson-type polyoxometalate ((C₄H₉)₄N)₆Mo₇O₂₄ and PVA [19], or potassium salt of the Cu-substituted phosphomolybdic acid (K₅PMo₁₁CuO₃₉, abbreviated as PMoCu), magnesium cuprate (MgCu₂O₄), and PVA [16], vanadium-substituted tungstoferrate (FeW₁₁V) and MMT modified with cetyltrimethylammonium bromide (CTAB) [50], modified with H₃PMo₁₂O₄₀ (PMA) imidazolium bromide C₃N₂H₅Br (IMIDBr), and chitosan [26], Fe₂W₁₈Fe₄@NiO@CTS nanocatalyst based on polyoxometalate (Fe₂W₁₈Fe₄), nickel oxide (NiO), and chitosan [51], Mn(II)-substituted heteropolyacids with Keggin-type-structured polyoxometalate (PMnW₁₁), titanium dioxide (TiO₂) and chitosan [52], CTAB-PTA@CS nanocatalyst based on cetyltrimethylammonium bromide (CTAB), phosphotungstic acid (PTA), and chitosan [49]. These NCs ensured the removal of 97% of sulfur from gasoline within 1–2 h at 35–60 °C with the initial sulfur content of ~500 ppm [52]. Similar results were obtained for other liquid fuel types (Table 2).

It was noted (Tables 1 and 2), that while using pure H₂O₂ even with the help of a 250 W high-pressure sodium lamp or microwave radiation the ODS takes longer time to reach acceptable desulfurization levels even at higher temperatures [61,65,71,74,75]. On the other hand, combining acetic acid with H₂O₂ allows performing efficient ODS at temperatures as low as 35 °C.

Ionic liquids (IL) are sometimes used as additional reagents for facilitating ODS [59,73]. The following ILs are considered as interphase mass transfer agents: quaternary ammonium salts (cetyltrimethylammonium bromide, tetrabutylimidazolium bromide, tetrabutylammonium bromide), as well as such compounds as butylimidazolium chloride hexadecylmethylimidazolium bromide, dodecylmethylimidazolium bromide, ethylmethylimidazolium bromide, isopropylmethylimidazolium bromide. It was noted that ILs can

also participate in the oxidation of the sulfur-containing compounds, possibly acting as a co-catalyst [78]. Thus, imidazole-based ILs can take an active part in oxidation of various derivatives of BT [64]. Complexes based on such ILs as $(C_{16}H_{33})_2N(CH_3)_2W_2O_{11}$ and N, N'-dialkylimidazolium salts of the type $[RMIM-Cl]_2$, where $[RMIM^+] = 1$ -alkyl-3-methylimidazolium and $M = Mn(II)/Fe(II)/Ni(II)/Co(II)$ were tested as precursors for thermal and chemical synthesis of NCs based on metal oxides [59,73]. Among the freshly prepared materials including the complexes based on ILs and metal oxide nanoparticles, thermally prepared metal oxides such as $\alpha-Fe_2O_3$, Mn_3O_4 , and Co_3O_4 had shown a high catalytic activity when preparing DBT, whereas those based on Co and Ni, such as $[EMIM-Cl][MnCl_2]$, $[EMIM-Cl][CoCl_2]$, and $[EMIM-Cl][NiCl_2]$, had a moderate catalytic activity [59].

As mentioned earlier, the polar oxidized compounds of sulfur can be separated from the fuel subjected to desulfurization (consisting mainly from non-polar hydrocarbons) via distillation, extraction, and adsorption [76,90]. Distillation cannot ensure the desired selectivity and has high energy requirements. Adsorption can be realized using silica gels, aluminium oxide, or zeolites, which can be regenerated via washing with organic solvents or calcinating the sulfones from the surface of the sorbent [91]. The essential drawback of these techniques is the unavoidable loss of hydrocarbon backbone of the sulfur-containing compounds and other components extracted from the fuel.

Extraction is an efficient and fast way of separating the sulfur-containing compounds from the reaction medium, which is sometimes combined with adsorption [88,92]. After the extraction the extractant can be regenerated via distillation. A wide range of substances can be used as extractants for removal of sulfur-containing compounds: acetonitrile (AN), N-methylpyrrolidone (N-MP), N,N-dimethylformamide (DMFA), ethyl acetate, ethylene glycol, γ -butyrolactone, 2-ethoxyethanol, ethylene glycol dimethyl ether, acetone, pyrrolidone, diglyme (diethylene glycol dimethyl ether), methanol, ethanol, isopropanol, as well as water and other substances [24,76,86,93]. Among this variety of extractants, only several allow achieving desulfurization levels above 90% for various model systems and real petroleum fractions due to the extraction of the oxidized forms of sulfur-containing compounds, while being available enough to be considered perspective. These include nitrogen-containing polar compounds such as AN, DMFA, and N-MP [94]. Though AN is currently by far the most widely used one among the extractants, several studies have shown that DMFA can ensure higher desulfurization levels [95]. Application of 1-butyl-3-methylimidazolium hexafluorophosphate for extracting sulfur-containing compounds has also shown good results, but this extractant has a relatively high cost [64].

The choice of extractants for ODS should also take into consideration minimizing the amount of non-sulfur containing hydrocarbons, which is extracted along with the sulfur-containing compounds. Extractants with lower polarity decrease the fuel quality due to a high degree of extraction of non-oxidized non-polar hydrocarbons. Therefore, it is expected that the losses of valuable hydrocarbons shall decrease in the following of series of nitrogen-containing extractants: AN, DMFA, and N-MP. It appears that in the course of a multi-stage process the sufficiently high degree of desulfurization of the raw materials can also be achieved with alcohols such as methanol, ethanol, and isopropanol [24,76,96].

Many NCs can be successfully separated from the reaction medium upon the completion of oxidation and extraction of the oxidized forms of sulfur, and can therefore be used for at least 3–5 cycles. This is an indisputably important feature when the perspectives of industrial application are considered [43,51,52,56,61,64,65]. For example, after the processes, the NCs can be separated with a simple filtration method, washed with ethanol or water and reused for several new runs [25]. Introduction of components with magnetic properties such as $MnFe_2O_4$ and Fe_3O_4 into the NCs extends the range of possibilities for complete extraction of the catalyst from the reaction system via using the magnetic field, thus preserving the NC for further re-use [25,65,75].

Thus a wealth of information has been accumulated on the mechanisms, possible realization, and modification of the ODS techniques for the stages of chemical oxidation

and extraction of sulfur-containing components from the fuel to be purified. The composition of the NCs in combination with oxidants and extractants has been optimized. Ways for enhancing the desulfurization efficiency have been suggested, e.g., due to the additional treatment with ultrasound or microwaves, photooxidation, or introduction of ILs, adsorbents, etc. into the reaction medium [2,18,97–99].

It was noted that many studies have been devoted to the search for environment-friendly and economically-efficient approaches to further use of extracts or sorbents containing adsorbed sulfur-containing compounds obtained in the course of ODS. One of the solutions found is the application of BCs at the final or additional stages of ODS (Table 3). The main features of such hybrid chemical-biocatalytic processes as compared to the known purely chemical techniques are the minimization of the environmental impact while preserving the economic efficiency and enhancing the resource and energy efficiency.

Table 3. Parts of hybrid chemical-biocatalytic desulphurization processes and components of heterogeneous catalysts.

Support (Carrier) for Catalysts	Oxidation of Sulphur-Containing Compounds	Biodestruction and Anaerobic Reduction of Sulphur-Containing Compounds	Green Bioconversion of Nitrogen-Containing Compounds
Chemical Catalysts (NCs)			
Mesoporous oxides (GO, TiO ₂ , SiO ₂ , PbO, Al ₂ O ₃ , etc.)			
Ceramic materials			
Mesostructured silicates (MCM-41, SBA-15, etc.)	Metals (Pd, Au, etc.)		
Natural microporous materials (zeolites, bentonites, montmorillonite, etc.)	Metal oxides		
Polymeric organic supports (polyvinyl alcohol (PVA), chitosan (CS), etc.)	Polyoxometalates (POMs)	-	-
Metal-organic frameworks (MOFs)	Other chemical compound types (molybdenum disulfide, etc.)		
Magnetic particles (Fe ₃ O ₄ , etc.)			
MicroBioCatalysts (BCs)			
Supports based on various polymers (PVA, CS, Ca-alginate gel, agar, K-carrageenan, etc.)	<i>Pseudomonas</i> sp.	Adapted anaerobic sludge Sulphate-reducing bacteria (such as <i>Desulfovibrio vulgaris</i>)	Adapted anaerobic sludge Anammox bacteria (such as <i>Candidatus rocadia sinica</i>)
Natural microporous materials (celite, zeolite, etc.)	<i>Rhodococcus</i> sp.		
Photocurable resins	<i>Gordonia</i> sp.		
(ENT-4000 and ENTP-4000, etc.)	<i>Nocardia</i> sp.	H ₂ -producing bacteria (such as <i>Clostridium acetobutylicum</i>)	
Magnetic particles (Fe ₃ O ₄ modified with oleate, etc.)	<i>Brevibacterium lutescens</i>		

Biocatalytic stages of the process almost always imply using rather mild conditions for their realization. The main point and difficulty in developing such environment-friendly hybrid processes is the seamless combination of the physicochemical and biological stages while preserving the target efficiency criteria.

The choice of oxidants, NCs, and extractants should take into account the subsequent biocatalytic stages, which shall ensure further transformation of sulfur-containing compounds. In turn, during the biocatalytic stage the conditions should be ensured to minimize the possible negative effect of the potential presence of chemical toxicants in the reaction medium.

3. The Choice of NCs, Extractants, and Oxidants for Use in Hybrid Chemical-Biocatalytic ODS Processes

The development of hybrid chemical-biocatalytic processes is of interdisciplinary nature. Therefore, evaluating the possibilities of combining various stages should account for a number of factors when choosing the suitable NCs and oxidant pair, the extractant for removing the oxidized forms of sulfur from the petroleum fractions, as well as other reagents involved.

3.1. Choosing Reagents Ensuring a High Desulfurization Efficiency and Compliant with the Green Chemistry Principles

First of all, the reagents used for ODS should be inexpensive, available, and environment-friendly, have high efficiency of oxidation and extraction of the sulfur-containing compounds from the treated raw materials. According to the Euro-5 (EN 590:2009) environmental standard, the main target parameter for evaluating the efficiency of the oxidation and extraction stages is the residual sulfur content in the refined fuel of below 10 ppm [9,45].

The analysis of the known achievements in ODS allows the conclusion that certain solutions of this problem are currently available based on application of NCs which, in combination with necessary oxidants and extractants, can ensure achieving the target efficiency of the process (Tables 1 and 2).

Hydrogen peroxide is a cheap and available reagent compliant with the principles of green chemistry and environment-friendliness. It can be obtained via an environment-friendly electrochemical technique involving oxygen reduction in a water solution [100]. Production of H_2O_2 in the course of isopropanol oxidation with oxygen is also environment-friendly enough. There are well-developed approaches to production of isopropanol from CO_2 or renewable raw materials (RRM) [101,102]. The advantage of the technique of H_2O_2 production from isopropanol is that acetone can be obtained in the same process.

The environment-friendly feature of the ODS processes based on the combination of H_2O_2 and formic or acetic acid is that these organic acids can be obtained from RRM (e.g., CO_2 and H_2) and waste (e.g., waste activated sludge biomass, agricultural waste, etc.) in the course of the green chemistry processes [103–107].

Techniques for obtaining the reagents from RRM are currently known for most of the substances which were suggested for use in ODS. Bioethanol is one of such RRM [108], which can also be used for producing AN via amination of the alcohol with ammonia [109,110]. Glutamic acid of biological origin is a potential raw material for obtaining N-methylpyrrolidone (N-MP). The intermediate products in this process include γ -aminobutanoic acid and 2-pyrrolidone [111]. Perspective and highly efficient approaches to producing N,N-dimethylformamide (DMF) from CO_2 , H_2 , and dimethylamine have been suggested [112]. The dimethylamine is usually obtained from ammonia and methanol nowadays. Production of ammonia requires N_2 (from atmospheric air) and H_2 (from synthesis gas). The techniques for producing synthesis gas and biomethanol from RRM are known, e.g., that via glycerin [113].

Thus, combinations of NCs, oxidizing reagents, and extractants have been suggested that ensure high an efficiency of liquid fuel desulfurization (Tables 1 and 2), while keeping perspective in terms of environment-friendliness and compliance with the principles of green chemistry.

3.2. Choosing Reagents with the Minimal Inhibiting Effect on the BCs and with the Potential of Bioconversion

While developing the hybrid ODS processes, in addition to the criteria mentioned above, it is necessary to take into account the possibility of certain chemicals involved in the chemical stages of the process getting into the bioreactor. These include the NCs themselves, the oxidized forms of sulfur, as well as the residual quantities of the oxidant. Therefore, the physicochemical stages of hybrid ODS techniques should use chemical reagents with the least possible inhibiting impact on the BCs and with a potential for bioconversion.

The NCs containing molybdenum and tungsten attract a lot of attention, because such compounds are known to be present in the feed media for culturing various microorganisms [114–116] and to have a positive impact on the overall ODS efficiency [24].

The choice of H_2O_2 as the primary oxidizer in developing hybrid processes is also well-founded. H_2O_2 is known to be actively used for the chemical treatment of various substrates including those intended for anaerobic conversion into biogas [117–119]. Additionally, H_2O_2 can act as an efficient disinfectant for the treated media [120]. However, upon oxidation of the sulfur-containing organic compounds in the hydrocarbon medium, hydrogen peroxide is converted into water. Therefore, low residual concentration of H_2O_2 (below 1 mL/L) in the solution obtained upon the extraction stage of the process can be ensured. As for other peroxide compounds used for ODS, the tert-butyl peroxide is known to be used in coatings and foams with antibacterial activity [121]. Therefore, the residual quantities of this oxidant in the extracts can have a negative impact on the activity of the BCs at the subsequent biocatalytic stages of ODS. Thus, the choice of H_2O_2 over other known peroxide oxidants appears to be reasonable for developing hybrid processes involving BCs.

The possibility of bioconversion of the abovementioned perspective extractants, sulfur-containing organic compounds, and other components that can get into the extracts from the treated hydrocarbon liquid fuel is a key issue for the development of the hybrid ODS processes. However, such a possibility is known to exist for all of the substances involved under certain conditions in an anaerobic bioreactor when BCs in the form of microbial consortia are used [24,122–125].

The potential commercial end product of the anaerobic conversion of the extracts containing oxidized forms of the organic sulfur-containing compounds is a biogas with a high content of methane. Such a gas is a perspective raw material for C-1 chemistry. The sulfur is transferred into the biomass or converted into sulfide in this process [24,45–47,126].

4. The Perspectives of Creating Hybrid Processes Based on ODS, Involving Microbial Biocatalysts, and Producing Substances Valuable for C-1 Chemistry

4.1. Chemical Conversion of the Sulfur-Containing Compounds during Oxidative or Reductive BDS

Involving BCs into catalytic processes connected with desulfurization is a perspective direction for the development of green chemistry. The current choices for BCs are cells and enzymes capable of chemical transformation of a wide range of organic sulfur-containing compounds under mild conditions [127–129].

The important point is that, depending on the targets of the process involving BCs, sulfur can be extracted from the hydrocarbon raw materials either in the oxidized form (as sulfates or sulfoxes) [130–132], or in the reduced one (as sulfides) [133,134] (Figure 1).

The mechanism of OBDS implies a series of reactions involving oxygen and known as the 4S-pathway (Figure 1), and ending with the production of compounds containing sulfur in an oxidized form [132,134–136]. This pathway was first described for *Rhodococcus erythropolis* IGTS8 bacteria [137], and later found for other BCs as well [138].

The classical 4S-pathway includes a 4-stage transformation of the heterocyclic sulfur-containing compound DBT via the consecutive formation of dibenzothiophene sulfoxide (with DszC monooxygenase as catalyst), dibenzothiophene sulfone (the same), 2'-hydroxydiphenyl-2-sulfinate (with DszA monooxygenase as catalyst) into 2-hydroxydiphenyl (2-HDP) and sulfite (with DszB desulfinate as catalyst) (Figure 1) [134,137]. Sulfite is then converted into sulfate under the action of sulfite reductase [138]. Additionally, three oxidation stages consume the reduced form of flavin mononucleotide, which is produced by flavin reductase (DszD) [139].

The reductive pathway of bioconversion of organic and inorganic sulfur-containing compounds, e.g., such electron acceptors as sulfates, sulfoxides, or sulfones, can be efficiently realized using certain BCs belonging to sulfate reducing bacteria (SRB), e.g., *Desulfovibrio* sp. An important advantage of BCs in the form of SRB is their wide range of catalytic fermentative activities induced in the presence of the substrate, which are specific

for various oxidized forms of sulfur, including heterocyclic organic compounds. It was noted that aromatic sulfur-containing compounds are more prone to reductive desulfurization compared to the aliphatic ones [140]. The participation of SRBs in the processes under anaerobic conditions ensures the removal of sulfur from the organic compounds in the sulfide form [45,47]. In the course of biocatalytic anaerobic biotransformation the C–S bond is destroyed, and the end products of the reaction are biphenyl and sulfide (Figure 1) [134]. In the course of reductive biodesulfurization following the methanogenesis pathway (Figure 1) free hydrogen or nitrogen, as well as certain organic substances such as lactate, ethanol, volatile fatty acids (the latter including acetic, propionic, and butyric) acids can be electron donors.

The extremely low reduction potential S^{+6} ($E^\circ = -0.454$ V for sulfate at pH 7) can be a crucial reason for the absence of known BCs which could have reduced S^{+6} to sulfite in a single stage. The adenosine triphosphate (ATP) molecule is the first to react with the oxidized sulfur-containing substrate, and the result of this reaction involving the ATP-sulfurylase is adenylylsulfate. Then in case of dissimilative pathway this product is converted to a sulfite due to the oxidation of cytochrome C3 under the action of adenylyl sulfate-reductase. Then sulfite reductase converts this product to a sulfide. In case of CH_2O being an organic reducing substance, the general form of the equation for the dissimilating reductive desulfurization can be written as follows:



In case of assimilating reduction pathway adenylyl sulfate is converted into phosphoadenylyl sulfate in a enzymatic process involving adenylylsulfate kinase. Then in the course of oxidation of nicotinamide adenine dinucleotide phosphate the sulfite is liberated and reduced to sulfide. The latter compound is subsequently involved into a chain of reactions connected with the synthesis of sulfur-containing amino acids, such as cysteine and methionine [141].

In order to enhance the efficiency of reductive desulfurization, in addition to SRBs, other BCs can be added to the working medium. These additional BCs should be capable of splitting the sulfur-containing polycyclic aromatic compounds into simpler ones, as well as ensuring the presence of reductive compounds in the reaction medium.

Biocatalytic consortia in the form of anaerobic sludge (AS) containing SRB are capable of processing the sulfur-containing compounds under anaerobic conditions and converting them into the same final product as the HDS does, namely, into sulfide [142]. The SRBs are known to help extracting greater amount of sulfur from the heavy petroleum fractions via the reductive pathway, than from the ray petroleum samples or from lighter fractions [143]. However such anaerobic processes take longer than the known aerobic processes. No data have been published on the BCs capable of directing reductive desulfurization of petroleum or model systems based on BT or DBT. Due to the low rate and high sensitivity to the inhibiting action of high concentrations of sulfide, the reductive biodesulfurization (RBDS) is not currently considered as a primary and separate technique for removing sulfur from the liquid fuels. However, unique fermentative activities of SRBs and other BCs present in the AS are of fundamental and practical interest for using such BCs in the hybrid processes of oxidative desulfurization of liquid fuels.

4.2. Advantages and Features of Applying IBCs for Desulfurization of Liquid Fuels

One of the main concerns in developing hybrid processes is minimizing the toxic impact of the components involved on the BCs, which makes immobilization of BCs the most reasonable solution for this problem [144]. Application of immobilized biocatalysts (IBCs) was found to increase the stability of the cells' functioning, to simplify the technique for separating the IBCs from the reaction medium, and to extend the possibility of their multiple applications in batch mode [144–147].

Immobilization via adsorption of specific BCs is a simple and effective approach to obtaining IBCs for further use in desulfurization processes (Table 4, [148–155]). In order

to produce IBCs via adsorption, similar to the case of producing immobilized NCs for the chemical processes, inexpensive non-toxic and available mineral carriers are most often used: silica, alumina, titanium oxide, sepiolite, etc. [90,156–158]. Among these carriers, independent on the BC type (*Pseudomonas* spp. or *Rhodococcus* spp.) the highest activity of the IBCs was observed in case of alumina and sepiolite [90,156,157]. Calcium alginate gel was successfully used for producing IBCs via inclusion (Table 4).

Table 4. Examples of using IBCs in OBDS processes via 4S-pathway.

Liquid Fuel	IBCs	Carrier/IBC Creation Technique	Process Conditions	OBDS Efficiency, Vs, T, [Ref.]
0.54 mM DBT in tetradecane (17 mg S/L)	<i>Rhodococcus erythropolis</i> KA2-5-2	Photocurable resins (ENT-4000 and ENTP-4000)/Inclusion	10 mL n-tetradecane + DBT (0.54 mM) + IBC, 30 °C, 20 h, 120 rpm	100%, 0.85 mg S/L/h, 900 h [148]
2.5 mM DBT in dodecane (80 mg S/L)	<i>Rhodococcus erythropolis</i> LSSE8-1	Magnetic nanoparticles of Fe ₃ O ₄ modified with oleate/Adsorption	20 mL water media with 10 g/L glycerin + 0.19 g IBC + 5 mL ISCM, 30 °C, 20 h, 180 rpm	100%, 4 mg S/L/h, 140 h (14 cycles) [149]
10 mM DBT in hexadecane (320 mg S/L)	<i>Gordonia</i> sp. CYKS1 or <i>Nocardia</i> sp. CYKS2	Celite/Adsorption	20 mL minimal salt water medium with 5 g/L glucose and IBC (50 vol %) + 1 mL ISCM, 24 h	40–78%, 5–10 mg S/L/h, 168–192 h (7–8 cycles) [150]
0.5–5 mM DBT in dodecane (16–160 mg S/L)	<i>Gordonia</i> sp. WQ-01A	Ca-alginate gel/Inclusion	41.9 mass % solution NaCl + DBT + IBC, 30 °C, 40–100 h, 200 rpm	100%, 0.4–1.6 mg S/L/h, 40–100 h [151]
3 mM (thiophene and DBT = 1:1) in m-octane (96 mg S/L)	<i>Pseudomonas delafieldii</i> R-8	Ca-alginate gel/Inclusion	2 mL of NaCl solution + 8 g IBC + 10 mL ISCM, 30 °C, 24 h, 180 rpm	25–40%, 2.4–3.8 mg S/L/h, 450 h (15 cycles) [152]
2.7 mM DBT in dodecane (86.4 mg S/L)	<i>Pseudomonas stutzeri</i> UP-1	Ca-alginate gel/Inclusion	40 mL of 0.9% solution of NaCl + 10 g IBC + 1 mL Tween 80 + 10 mL ISCM, 31 °C, 24 h, 200 rpm	74%, 2.7 mg S/L/h, 600 h [153]
2.7 mM DBT (86.4 mg S/L)	<i>Pseudomonas stutzeri</i> UP-1	Ca-alginate gel/Inclusion	50 mL water medium + 10 g IBC + DBT in 200 µL DMFA, 31 °C, 24 h, 200 rpm	65%, 2.3 mg S/L/h, 600 h [153]
0.88 mM DBT (28 mg S/L)	<i>Pseudomonas stutzeri</i>	Ca-alginate gel/Inclusion	100 mL model diesel +10 g IBC + 9 mL of phosphate buffer, 35 °C, 48 h, 120 rpm	82%, 0.48 mg S/L/h, 48 h [154]
0.54 mM DBT in tetradecane (17 mg S/L)	<i>Pseudomonas</i> sp. strain KWN5	Ca-alginate gel/Inclusion	17.5 mL saline solution + 2.5 mL ISCM, 37 °C, 24 h, 160 rpm	100%, 0.7 mg S/L/h, 24 h [155]

Vs—desulfurization rate; T—desulfurization duration; ISCM—initial sulfur-containing medium.

According to the scanning electron microscopy data, Ca-alginate capsules had a spherical shape, and the cells were completely isolated from the environment with a thin layer of gel. However in case of using polysaccharide-containing gels (Ca-alginate or agar) as a matrix for obtaining IBCs via inclusion of *Rhodococcus erythropolis* KA2-5-1 cells leaching of the latter from the carrier matrix and a low mechanical stability of the carrier were observed [148]. A reliable attachment of the BC and a high desulfurization activity were ensured by the additionally applied ENT-4000 prepolymer; the service life of such IBC was 900 h (Table 4).

PVA cryogel was successfully tested as support for producing IBCs capable of participating in ODS processes [24,45–47,126,159]. An essential feature of the PVA cryogel-based IBCs is the possibility of repeated application and long-term storage without a loss of catalytic activity [126].

Biocatalysis differs in several essential features from the classical chemical catalysts, and these features should be taken into account when developing IBCs based on cell cultures and looking for ways to optimize the corresponding processes. It is important to remember that IBC is a holistic system that can often ensure a rather fast completion of a chain of interconnected biochemical reactions, which is now always possible for chemical NCs. However, controlling these processes is a more difficult task, because the activity and the efficiency of the IBCs depend on a larger number of factors than in case of chemical catalysis.

Many physical, chemical, and other factor influencing the activity and other characteristics of IBCs only come to light for the first time in the experiments while studying the possibilities of developing new hybrid processes for desulfurization of liquid fuels.

Thus, not only is the impact of such obvious parameters as composition of the carrier matrix and the technique for producing IBCs studied in order to optimize the OBDS, but also that of IBC particle size and mode (periodic or continuous) of the biocatalytic process.

The nature of the cells used in IBCs also plays an important role, as does the possibility of these cells for enhancing the efficiency and convenience of using IBCs, etc. Note, that even in view of the specific feature of the biocatalysts, the catalytic characteristics of IBCs can often still be described in terms of classical techniques for studying kinetics and catalysis [144,145].

Studying the influence of the IBC granule size for *Pseudomonas delafieldii* R-8 cells included in Ca-alginate gel on OBDS process for model fuel [152] has shown that decreasing the granule diameter from 4.0 to 1.5 mm allowed increasing the bioconversion rate for DBT by a factor of 1.4 (to 1.36×10^{-2} mM/h) [156].

Note that the microorganism cells forming the IBCs, such as, e.g., *Rhodococcus erythropolis*, can secrete surfactants ensuring solubilization of the fuel, which increases the rate of the chemical processes stimulated by these cells [148].

Up to now much information has been published on using BCs for desulfurization of fuels, both model ones (most often containing BT or DBT and their derivatives) and real media (gasoline fractions, diesel oil, gasoil, etc.) [24,46,127–129].

The transition from model fuels to real fuel samples can cause either an increase or a decrease in the process rate. Light gasoil contains various easy to desulfurize compounds such as thiols and sulfides [150], so the OBDS rate for this liquid fuel type was 4–7 times higher than that for the model liquid fuel containing DBT [158]. An opposite effect was observed when performing OBDS of vacuum gasoil and bitumen [140].

The influence of the carrier particle size on DBT degradation in gasoil was studied for OBDS in a flow bioreactor with IBC based on silica and *Rhodococcus rhodochrous* [160]. It was established that the rate of DBT degradation was higher when particles from different size ranges (0.71–1.18 mm or 3.35–5.6 mm) were used than when the bioreactor contained only larger IBC particles. The possibility of IBC regeneration after a separate operation cycle was shown. The desulfurization efficiency under flow conditions for the maximum retention time was 18%.

Modification of IBCs via inclusion of magnetic particles essentially enhances the practical importance of the processes involving such biocatalysts. Such IBCs can be easily separated from the reaction medium using a magnetic field. It was shown that co-precipitation technique can yield a hydrophilic carrier in the form of magnetic nanoparticles based on Fe_3O_4 covered with ammonium oleate [149]. Adsorption of *Rhodococcus erythropolis* LSSE8-1 cells on such carrier can easily produce an efficient IBC (Table 4). Oleic acid, as well as amino acids, can be used for building the carrier matrix for immobilizing BCs. These substances are potentially important for developing green chemistry processes, be-

cause they can be produced from RRM, in particular, from microalgae biomass which is accumulated in the course of wastewater treatment [161].

Note also that the magnetic Fe_3O_4 particles are widely used in modern innovative techniques, e.g., connected with developing new systems for targeted transport of drugs and biomolecules [161]. Their application for producing new IBCs for desulfurization is of great fundamental and practical importance, and can contribute to solving the environmental problems connected to biological waste management.

A modified IBC based on *Pseudomonas delafieldii* included via the borate technique in a PVA cryogel containing magnetic particles was studied [162]. The gel granules also had superparamagnetic properties. The OBDS activity of such IBC was preserved even after the 7th application cycle, whereas similar biocatalysts without magnetic particles were difficult to separate from the reaction medium and could be re-used for desulfurization no more than five times.

Application of the combination of magnetic particles and cryotropic gel-formation for immobilizing *P. delafieldii* R-8 to produce magnetic PVA cryogel capsules has been studied [163]. This technique allowed enhancing the stability of the cells' functioning and increasing the number of possible re-use cycles up to 12. The maximum process rate (0.402 mM S/L/h) for this IBC was higher than that in case of free cells (0.295 mM S/L/h).

Biotransformation of DBT was also performed with *Brevibacterium lutescens* CCZU12-1 cells included in Ca-alginate cells with magnetic nanoparticles based on Fe_3O_4 [164]. Using DBT as the only source of sulfur, this IBC could transform DBT to 2-HDP via the 4S-pathway. The IBC based on *B. lutescens* spp. could be re-used at least four times.

All the approaches to modification and stabilization of IBCs used for OBDS via the 4S-pathway can also be applied for processes connected with biotransformation of sulfur-containing organic compounds by anaerobic IBCs. The following carriers were successfully tested for creating anaerobic IBCs: activated carbon, silica gel, expanded clay, zeolite, synthetic and natural polymers such as polyethylene, CS, PVA, agar, carrageenan, etc. [45,126,165]. Anaerobic IBCs based on PVA cryogel were up to 2.5 times more efficient in bioconversion of sulfones into sulfide than those used in suspended form. The degree of sulfone decomposition and sulfide output was 100% after 18 days of bioconversion of 0.15–0.45 mM DBTO₂ under anaerobic conditions using immobilized AS chosen upon preliminary screening and water, ethyl and isopropyl alcohol as model extractants. It was shown that in the course of bioconversion of organic sulfones (BTO₂ or DBTO₂) it was possible not only to convert the sulfur contained in the organic compound, but also to produce biogas under anaerobic conditions. The methanogenesis efficiency of this process can be as high as 100% [47].

Thus, the analysis of the data accumulated up to date on the specific features of creating and applying IBCs for desulfurization allows the consideration of various approaches to involving such IBCs in hybrid ODS processes. IBCs with oxidative potential towards sulfur-containing compounds via OBDS can be applied for deeper purification of the materials obtained upon completion of chemical ODS. The IBCs with reductive potential can ensure a rather low rate of anaerobic biotransformation of sulfur-containing substances in hybrid ODS processes. Therefore, it is reasonable to apply such IBCs at the stage of bioconversion of the oxidized forms of sulfur in order to produce materials for C-1 chemistry.

4.3. IBC-Induced Biotransformation of Oxidized Forms of Sulfur-Containing Compounds under Anaerobic Conditions

The desulfurization products such as sulfides and certain monomers (in particular, organic acids of biocatalytic origin, such as lactic, succinic, fumaric, aspartic, malic, etc.) are considered as perspective raw materials in the frame of green chemistry concept. These materials can be used for developing new approaches in polymer chemistry and producing functional materials [24,166]. It was established that anaerobic sludge (AS) can be used as a universal BC for converting various oxidized forms of sulfur-containing organic compounds present in model and real media (Table 5).

Table 5. Application of IBCs in the form of cells immobilized in PVA cryogel in the processes of reductive biotransformation of oxidized forms of organic compounds.

Extract Containing Oxidized Sulfur; IBC	Process Conditions	Vs,mg S/L/h	T, h	Methano-Genesis Efficiency, %	CH ₄ Content, [Ref.]
0.15 mM BTO ₂ in ethanol (48 mg S/L), AS	0.1 M K-phosphate buffer (pH 7.2) + BTO ₂ + glucose (1 g/L) + IBC, 35 °C, 8 days	0.6	192	100	66% [47]
0.45 mM DBTO ₂ in ethanol (14.4 mg S/L), AS	0.1 M K-phosphate buffer (pH 7.2) + DBTO ₂ + glucose (1 g/L) + IBC, 35 °C, 18 days	0.8	432	100	65% [47]
0.45 mM DBTO ₂ in ethanol (14.4 mg S/L), 80% AS III + 10% <i>D. vulgaris</i> + 10% <i>C. acetobutylicum</i>	0.1 M K-phosphate buffer (pH 7.2) + DBTO ₂ + glucose (1 g/L) + IBC, 35 °C, 8 days	1.8	576 (3 cycles)	100	82% [47]
Methiocarb sulfone (0.4 mg S/L), AS	0.1 M K-phosphate buffer (pH 7.2) + Methiocarb sulfone + hydrolysate of Jerusalem artichoke stems (3 g COD/L) + IBC, 35 °C, 19 days	-	456	87	73% [126]
0.15 mM BTO ₂ in ethanol (4.8 mg S/L), 80% AS + 10% <i>D. vulgaris</i> + 10% <i>C. acetobutylicum</i>	0.1 M K-phosphate buffer (pH 7.2) + BTO ₂ + glucose + IBC, 35 °C	-	-	99	63% [45]
	0.1 M K-phosphate buffer (pH 7.2) + BTO ₂ + hydrolysates of <i>C. vulgaris</i> biomass + IBC, 35 °C	-	-	98	64%, [45]
Naphtha ODS extract in ethanol (2 mg S/L), 80% AS + 10% <i>D. vulgaris</i> + 10% <i>C. acetobutylicum</i>	0.1M K-phosphate buffer (pH 7.2) + Naphtha + glucose (3 g COD/L) + IBC, 35 °C	0.2	240	30.0	74% [24]
	Naphtha + wheat straw (3 g COD/L) + IBC, 35 °C	0.2	240	29.4	72% [24]
	Naphtha + aspen sawdust (3 g COD/L) + IBC, 35 °C	0.2	240	19.8	77% [24]
	Naphtha + <i>Chlorella vulgaris</i> biomass (3 g COD/L) + IBC, 35 °C	0.2	240	20.2	62% [24]

The conversion of sulfones into sulfide can be intensified via forming artificial consortia by enriching the AS with supplementary IBCs in the form of immobilized cells of SRB (such as *D. vulgaris*) or H₂-producing bacteria (such as *C. acetobutylicum*).

In order to successfully transform both model and real media and achieve 100% bioconversion of the oxidized forms of sulfur an artificial consortium containing the following three basic components: AS, *D. vulgaris*, and *C. acetobutylicum* can be formed (Table 5). This consortium can be reliably reproduced and efficiently immobilized to enhance its efficiency. The AS should be chosen from the consortia used for the treatment of wastewater containing, in particular, sulfates, because such AS is well adapted to the bioconversion of the oxidized forms of sulfur-containing compounds. It is important that introducing this IBC into the anaerobic bioreactor while controlling the pH of the reaction medium at the level of 7.0–7.2 allows both to reduce the oxidized forms of sulfur to sulfides and to produce biogas with a high content of CH₄ (60–80%). Moreover, this biogas shall

contain almost zero H_2S , because under controlled conditions the sulfide tends to remain in the liquid phase (Table 5).

The advantage of the hybrid processes of chemical-biocatalytic desulfurization is the possibility of biotransformation of not only the sulfur-containing substrates, but also the bioorganic waste as the raw material. It was established that hydrolysates of the *Chlorella vulgaris* microalgae biomass remaining upon extraction of lipids, as well as those of Jerusalem artichoke and wheat straw, can be a co-substrate capable of yielding biogas in the presence of IBC and oxidized forms of sulfur-containing organic compounds [24,45,126]. It was shown that the IBCs in the form of anaerobic cells (AS, *D. vulgaris*, *C. acetobutylicum*) immobilized in PVA cryogel can be reused for at least three cycles. The PVA cryogel matrix is stable against mechanical, chemical, and microbiological influence and can thus ensure a long service life of such BCs.

Note that application of microbial biocatalysts helps solving the problems of environment-friendly processing of nitrogen-containing components of the waste, such as nitrogen-containing organic compounds, ammonium salts, and nitrates. These can be converted into N_2 or NO_2 with the help of additional IBCs, namely, with anammox bacteria [167–169].

4.4. Specialized Adaptive and Complex Approaches to Involving IBCs in Hybrid ODS Processes

Independent on the chosen way of desulfurization of petroleum and oil products the main criteria for evaluating the efficiency of IBCs and the processes involving the biocatalysts remain the same. These are: the percentage of sulfur removed from the liquid fuel, the destructive activity of BCs towards hydrocarbons, the desulfurization rate (V_s), the possibility of long-term/multiple use/storage of the IBCs, the range of permissible initial sulfur content in the raw material, and the economic and environmental efficiency.

In addition to immobilizing the BCs and choosing the most suitable reagents for the chemical oxidation and extraction stages, several other approaches are known to facilitate achieving the target efficiency parameters when realizing the hybrid ODS process [24].

Taking into account the qualitative composition of the sulfur-containing extracts of ODS for their biotransformation to biogas and sulfide certain artificial microbial consortia can be formed in order to achieve the target efficiency characteristics of the hybrid process. Such consortia, e.g., can be based on AS, *Clostridium acetobutylicum*, and *Desulfovibrio vulgaris* [24]. In order to ensure biotransformation of hydrocarbon components, oil-degrading cells can be introduced into the consortia, such as *Rhodococcus* sp. If a certain “unconventional” substrate, e.g., DMFA, is present in the extracts, then the way to enhance the efficiency of the consortium is mixing anaerobic and aerobic sludge with a high fermentative activity of dimethylformamidase (DMFase) [123]. Preliminary induction of the target activity of the IBC can also be applied via exposing it to a medium containing sulfur compounds (e.g., DBT), possibly with a lower concentration [149]. Thus, IBC based on *Rhizopus nigricans* mycelial fungus was preliminarily adapted to processing sulfur-containing compounds via cultivation in a medium containing $\text{Na}_2\text{S}_2\text{O}_5$. Upon the adaptation this IBC (under optimal conditions) could process more than 90% of the sulfur-containing compounds in the filtrate obtained after the treatment of petroleum with a water solution of H_2SO_4 at 80°C within 3 h [170].

Once the artificial consortium has been formed, the anaerobic microorganisms of such consortium can be gradually adapted to the presence of components which are otherwise toxic for these cells [126]. The toxicity of the extracts before introducing them into the bioreactor can be evaluated via a bioanalytical technique using PVA cryogel-immobilized *Photobacterium* cells [171–174]. An optimal solution concentration for the extracts can be chosen, if necessary, to minimize the inhibiting effect of the chemical components therein on the biocatalytic activity of the participants of the microbial consortium [24]. The metabolic activity of the BCs in the course of biotransformation of sulfones can be evaluated via the concentration of the intracellular adenosine triphosphate (ATP) [47,126].

Note that the desulfurization rate can increase from cycle to cycle for various reasons, the main one being BC cell proliferation within the carrier. Thus, the initial concentration

of the IBC cells at the start of the first cycle was 1.5 mg BC/g carrier, whereas upon the completion of the 8th cycle it was 4.3 mg BC/g carrier [156].

In case of the decrease of its catalytic activity, the biocatalyst can be regenerated via extraction of the IBC from the reaction medium and transferring it into one with a composition optimal for recovering the target activity level. After such regeneration, the IBC can be re-used for biotransformation of sulfur-containing extracts. In order to support the catalytic activity of the IBCs, supplementary co-substrates can be introduced into the reaction medium to act as additional sources of carbon, nitrogen, as well as other macro- and microelements. Note that hydrolysates of various RRM of plant origin can be used as such co-substrates, as well as those of microalgae biomass accumulated in the course of wastewater treatment [45,175]. This can be an important step towards implementing the green chemistry principles.

Additional ultrasound treatment, introduction of surfactants, flocculants, and ionic liquids has a positive impact on the desulfurization efficiency involving IBCs. Thus, a process has been suggested for desulfurization of model fuel involving ultrasound treatment and biodesulfurization via the 4S-pathway using IBCs based on *Rhodococcus rhodochrous* cells adsorbed on polyurethane granules [176]. The analysis of the kinetic characteristics as well as the results of modeling the dynamics of cavitation bubbles allowed discovering the synergy between the ultrasound effects, cavitation, and efficiency of IBC functioning.

Adding non-ionogenic surfactants to the reaction medium allowed, essentially, increasing the biodesulfurization rate via the 4S-pathway in the course of the transformation of DBT to 2-hydroxydiphenyl under the action of IBCs based on *Rhodococcus erythropolis* R1 bacterial cells included into Ca-alginate gel granules. This effect was explained by the increase in the efficiency of DBT mass transfer between different phases caused by the surfactants [177].

Addition of surfactants containing 0.5% of Span 80 to the reaction medium was shown to increase the desulfurization rate by a factor of 1.8. The efficiency boost depended on the surfactant type and decreased in the following series: Span 80 > Tween 20 > Span 20 > Tween 80 = Triton X-100 > sodium dodecyl sulfate > cetyltrimethylammonium bromide. Introduction of natural or synthetic surfactants into the reaction medium, e.g., of lyophilisate of the culture of *Cobetia marina* MM1A2H bacterial species of marine origin or Tween 80 while using IBCs based on *Pseudomonas delafieldii* R-8 cells and Ca-alginate gel allowed increasing the desulfurization rate by a factor of 2–3 [156].

The metabolism of BCs used in combination in an IBC can be different from that of the same biocatalysts when applied separately. The efficiency of the anaerobic IBCs made of artificially created consortia can be monitored and optimized via controlling various important characteristics of the process. These include reaction medium pH, excess pressure due to accumulation of hydrogen, as well as the concentration of acetic, propionic, and butyric acids. The latter are intermediate compounds in a complex chain of chemical reactions and electron donors for those involved in reducing the sulfur-containing compounds. All these parameters are important indicators of the chemical status of the IBCs, especially in the case when a complex microbial consortium is chosen as the main catalytic component of the IBC, and the products of reactions involving some of the BCs are in their turn substrates for the activity of other biocatalysts. The pH and the concentration of the organic acids influence the activity of the most sensitive BCs in the anaerobic consortium: obligate hydrogen-producing acetogens and acetoclastic methanogens. The instability in the current concentration of the organic acids in the liquid phase causes an unbalance in the reaction rate between the two BC groups, namely, acidogens and methanogens. This imbalance is due to the difference in the physiology, nutrition requirements, growth kinetics, and the sensitivity towards the environmental conditions [178].

The organic acids have a strong influence on the metabolic processes occurring within the AS [144]. The higher concentrations of organic acids accumulated during the first stage of methanogenesis are known to inhibit the continuation of methanogenesis. Thus,

it was established that in a UASB reactor for wastewater treatment after the processing of cassava the concentration of organic acids of 8.8 g/L and 0.35 g/L inhibits the activity of hydrogen-producing bacteria and methanogenic ones, respectively, in the anaerobic consortium [179].

The analysis of the published information allows concluding that application of the above-described approaches can facilitate introducing IBCs into the hybrid ODS processes. However, there is still a wide range of issues open for continuing research in this topical and perspective field oriented at environmental friendliness and achieving high efficiency of liquid fuel desulfurization.

5. Conclusions

Thus a great body of information has been accumulated up to date on the possibilities of optimizing the functioning of IBCs while developing hybrid processes for oxidative desulfurization of liquid fuel.

Achieving the target environmental and economic criteria when developing new hybrid chemical-biocatalytic desulfurization processes is possible only via a complex analysis of a variety of technological schemes with “zero” waste, starting with the initial raw materials and going through to the possibility of obtaining a wide range of commercial products. The “environmental efficiency” in this case can be understood as achieving a positive net effect in terms of environmental, social, and economic practicability. So far, the latter is the main limiting factor for introducing environment-friendly techniques for making socially important mass consumption products while involving waste and renewable raw materials in the production cycle. Enhancing the economic attractiveness and the marketing potential of the hybrid schemes is possible only when at least a part of the chemical compounds produced in this way are components for innovative products with high surplus value, e.g., those for the medicine, pharmaceuticals, IT, or space industry [161]. Thus, achieving the environmental efficiency is possible for the general approach to such hybrid processes involving waste valorization. Such approaches have the best chances for practical realization in the near future.

In general, the approach to desulfurization of various hydrocarbon raw materials based on combining chemical oxidation involving NCs and biotechnological anaerobic reduction of the oxidized forms of sulfur obtained in the previous process can become a promising alternative to the known techniques for desulfurization of the petroleum products (Table 6).

The biotechnological stage involving IBCs can enhance both the rate and the efficiency of the total desulfurization process and thus give a boost to worldwide acceptance of hybrid approaches on the industrial scale. From an economic point of view, the hybrid process has real potential. The cost of fuel purification by the ODS depends significantly on the initial sulfur content, the type of oxidizer used, and also the type of NCs. The application of anaerobic BCs for the treatment of extracts with sulfur-containing compounds, which can be obtained after NCs application, allows obtaining clean oil and deep conversion of all components of the extracts into biogas (gaseous fuel) with obtaining of liquid medium with nonorganic sulfide. Since this hybrid process can be characterized by less disadvantages (Table 6) as compared to other variants of this process, it can be attractive for practice realization. There are no needs for special reactors with anaerobic BCs since the existing methane-tanks can be used. The additional optimization of conditions for hybrid process functioning can be applied to maximally improve it.

Table 6. The advantages and disadvantages of chemical and biocatalyst process including in the view of the hybrid chemical-biocatalytic processes.

Process Desulfurization of Liquid Fuels	Advantages	Disadvantages
Chemical process of Hydrodesulfurization (HDS)	<ul style="list-style-type: none"> * Effective for removal of aliphatic and acyclic sulfur-containing compounds * Sulfur is a potential product from waste * Low time costs 	<ul style="list-style-type: none"> * Problems for removal of polyaromatic sulfur-containing molecules * High operating costs to decrease sulfur concentration to 10–50 ppm
Chemical process of Chemical oxidative desulfurization (ODS) with NCs	<ul style="list-style-type: none"> * Effective for removal of all sulfur-containing compounds * Low time, technique, and energy costs * Green reagents * Selective oxidation of sulfur * Meet the strict requirements of the modern environmental standards 	<ul style="list-style-type: none"> * Sulfur-containing extracts as waste
Biocatalyst process of Oxidative biodesulfurization (OBDS)	<ul style="list-style-type: none"> * Green reagents * Meet the strict requirements of the modern environmental standards 	<ul style="list-style-type: none"> * High time costs * Inhibition of the biocatalyst by the product * Sulfur-containing extracts as waste
Hybrid chemical-biocatalyst redox processes	<ul style="list-style-type: none"> * Selective oxidation of sulfur * Effective for fast removal of all sulfur-containing compounds * Sulfur and biogas are potential products after biotransformation of waste * Green reagents * Meet the strict requirements of the modern environmental standards 	<ul style="list-style-type: none"> * High time costs for biocatalytic stage

Author Contributions: Conceptualization, E.E.; methodology, A.A. (Alexander Anisimov), S.L. and E.E.; validation, O.M. and O.S.; investigation, A.A. (Argam Akopyan), O.M., and O.S.; data curation, E.E.; writing—original draft preparation, O.M., O.S., A.A. (Argam Akopyan), S.L., and E.E.; writing—review and editing, O.M., O.S., A.A. (Alexander Anisimov), and E.E.; visualization, O.M., O.S. and A.A. (Argam Akopyan); supervision, E.E.; project administration, E.E. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by State Task of Lomonosov Moscow State University (AAAA-A21-121011290089-4) (the Sections 4.1 and 4.2) and Russian Foundation of Basic Research (18-29-05064) (all the rest Sections of the work).

Data Availability Statement: The data presented in this study are available by request.

Acknowledgments: This research was performed according to the Development program of the Interdisciplinary Scientific and Educational School of Lomonosov Moscow State University “The future of the planet and global environmental change”.

Conflicts of Interest: The authors declare no conflict of interest.

List of Acronyms

AS	anaerobic sludge
AN	acetonitrile
BC	biocatalyst
BTC	1,3,5-benzen-tricarboxylate
BDS	biodesulfurization
BNT	sodium activated bentonite
Bmin	1-butyl-3-methylimidazolium
BT	benzothiophene
BTC	benzene 1,3,5-tricarboxylate
BTO ₂	benzothiophene sulfone
CH ₃ CN	acetonitrile
CH ₃ COOH	acetic acid
CS	chitosan
CTAB	cetyltrimethylammonium bromide
DBT	dibenzothiophene
DBTO ₂	dibenzothiophene sulfone
4,6-DMDBT	4, 6-dimethyl dibenzothiophene
DMF	dimethylformamide
DMFA	N,N-dimethylformamide
Fe ₂ W ₁₈ Fe ₄	tetranuclear sandwich-type polyoxometalate
(Na ₉ K[(FeW ₉ O ₃₄) ₂ Fe ₄ (H ₂ O) ₂] ₃₂ H ₂ O	
GO	graphene oxide
HDS	
hydrodesulfurization	
HKUST-1	(Cu ₃ (BTC) ₂
H ₂ O ₂	
hydrogen peroxide	
H ₂ SO ₄	sulphuric acid
HPA	hetero Poly Acid
IBC	immobilized biocatalyst
IMID	imidazolium C ₃ H ₄ N ₂
ISCM	initial sulfur-containing medium
KTHPA	Keggin-type heteropolyanion [PW ₁₂ O ₄₀]
mGO	
modified graphene oxide	
MIL-101	MOF based on polymeric terephthalate
MMT	
montmorillonite	
MOF	
metal-organic frameworks	
NC	
Nanocatalyst	
N-MP	N-methylpyrrolidone
ODS	
chemical oxidative desulfurization	
OBDS	oxidative biodesulfurization
PMo	
H ₃ PMo ₁₂ O ₄₀	
PMo/HKUST-1	(Cu ₃ (1,3,5-benzen-tricarboxylate) ₂ H ₃ PMo ₁₂ O ₄₀ ,
POM	polyoxometalate
PTA	phosphotungstic acid,
PVA	polyvinyl alcohol
PWA	phosphotungstic acid
PW ₁₁ Zn	TBA4.2H ₂ O.8[PW ₁₁ Zn(H ₂ O)O ₃₉] ₅ H ₂ O
PW	H ₃ PW ₁₂ O ₄₀
RRM	renewable raw materials
SBA-15	Mesoporous Silica Molecular Sieve SBA-15

S_0	initial sulfur concentration
SiW	$H_3SiW_{12}O_{40}$
SO _x	sulfur oxides
SO ₂	sulfur dioxide
T	desulfurization duration,
TBA	tetrabutylammonium ($n-C_4H_9$) ₄ N
TH	thiophene
t-B.PWFe	$[n-C_4H_9]_4N_4H[PW_{11}FeO_{39}]$
TBA-SiWMn	Silicotungstate polyoxometalate
Vs	$((n-C_4H_9)_4N)_7H_5Si_2W_{18}Mn_4O_{68}$
	desulfurization rate

References

- Prajapati, R.; Kohli, K.; Maity, S.K. Slurry phase hydrocracking of heavy oil and residue to produce lighter fuels: An experimental review. *Fuel* **2021**, *228*, 119686. [\[CrossRef\]](#)
- Betiha, M.A.; Rabie, A.M.; Ahmed, H.S.; Abdelrahman, A.A.; El-Shahat, M.F. Oxidative desulfurization using graphene and its composites for fuel containing thiophene and its derivatives: An update review. *Egypt. J. Pet.* **2018**, *27*, 715–730. [\[CrossRef\]](#)
- Akhmadova, K.K.; Makhmudova, L.S.; Abdulmezhidova, Z.A.; Krasnikov, P.E.; Idrisova, E.U.; Magomadova, M.K. Oxidative methods of desulfurization of diesel fuels: Results, problems, perspective. *Adv. Eng. Res.* **2018**, *177*, 422–431.
- Saleh, T.A. Characterization, determination and elimination technologies for sulfur from petroleum: Toward cleaner fuel and a safe environment. *Trends Environ. Anal. Chem.* **2020**, *25*, e00080. [\[CrossRef\]](#)
- Houda, S.; Lancelot, C.; Blanchard, P.; Poinel, L.; Lamonier, C. Oxidative desulfurization of heavy oils with high sulfur content: A review. *Catalysts* **2018**, *8*, 344. [\[CrossRef\]](#)
- Stylianou, M.; Vyrides, I.; Agapiou, A. Oil biodesulfurization: A review of applied analytical techniques. *J. Chromatogr. B* **2021**, *1171*, 122602. [\[CrossRef\]](#) [\[PubMed\]](#)
- Ma, S.; Chai, J.; Wu, K.; Xiang, Y.; Jia, S.; Li, Q. Experimental research on bypass evaporation tower technology for zero liquid discharge of desulfurization wastewater. *Environ. Technol.* **2019**, *40*, 2715–2725. [\[CrossRef\]](#)
- Rezvani, M.A.; Shaterian, M.; Aghmasheh, M. Catalytic oxidative desulphurization of gasoline using amphiphilic polyoxometalate@ polymer nanocomposite as an efficient, reusable, and green organic–inorganic hybrid catalyst. *Environ. Technol.* **2020**, *41*, 1219–1231. [\[CrossRef\]](#)
- Fallah, R.N.; Azizian, S.; Dwivedi, A.D.; Sillanpää, M. Adsorptive desulfurization using different passivated carbon nanoparticles by PEG-200. *Fuel Process. Technol.* **2015**, *130*, 214–223. [\[CrossRef\]](#)
- Kulsing, C.; Rawson, P.; Webster, R.L.; Evans, D.J.; Marriott, P.J. Group-type analysis of hydrocarbons and sulfur compounds in thermally stressed mercox jet fuel samples. *Energy Fuels* **2017**, *31*, 8978–8984. [\[CrossRef\]](#)
- Kadijani, J.A.; Zolfaghari, A. Examining a catalyst sample for demercaptanization process. *Petrol. Sci. Technol.* **2019**, *37*, 2391–2396. [\[CrossRef\]](#)
- Motahari, K.; Abdollahi-Moghaddam, M.; Rashidi, A. Mechanism study and determination kinetic of catalytic oxidation of mercaptans in Merox process. *S. Afr. J. Chem. Eng.* **2020**, *33*, 116–124. [\[CrossRef\]](#)
- Li, M.; Zhang, M.; Wei, A.; Zhu, W.; Xun, S.; Li, Y.; Li, H.; Li, H. Facile synthesis of amphiphilic polyoxometalate-based ionic liquid supported silica induced efficient performance in oxidative desulfurization. *J. Mol. Catal. A Chem.* **2015**, *406*, 23–30. [\[CrossRef\]](#)
- Shen, L.; Lei, G.; Fang, Y.; Cao, Y.; Wang, X.; Jiang, L. Polymeric carbon nitride nanomesh as an efficient and durable metal-free catalyst for oxidative desulfurization. *Chem. Comm.* **2018**, *54*, 2475–2478. [\[CrossRef\]](#) [\[PubMed\]](#)
- Yang, H.; Jiang, B.; Sun, Y.; Zhang, L.; Sun, Z.; Wang, J.; Tantai, X. Polymeric cation and isopolyanion ionic self-assembly: Novel thin-layer mesoporous catalyst for oxidative desulfurization. *Chem. Eng. J.* **2017**, *317*, 32–41. [\[CrossRef\]](#)
- Rezvani, M.A.; Shaterian, M.; Akbarzadeh, F.; Khandan, S. Deep oxidative desulfurization of gasoline induced by PMoCu@MgCu₂O₄-PVA composite as a high-performance heterogeneous nanocatalyst. *Chem. Eng. J.* **2018**, *333*, 537–544. [\[CrossRef\]](#)
- Eseva, E.; Akopyan, A.; Schepina, A.; Anisimov, A.; Maximov, A. Deep aerobic oxidative desulfurization of model fuel by Anderson-type polyoxometalate catalysts. *Catal. Commun.* **2021**, *149*, 106256. [\[CrossRef\]](#)
- Sinhmar, P.S.; Gogate, P.R. Ultra-deep desulfurization of crude sulfated turpentine using oxidation, adsorption and novel combination approach. *Environ. Technol. Innov.* **2020**, *18*, 100682. [\[CrossRef\]](#)
- Rezvani, M.A.; Asli, M.A.N.; Oveisi, M.; Babaei, R.; Qasemi, K.; Khandan, S. An organic–inorganic hybrid based on an Anderson-type polyoxometalate immobilized on PVA as a reusable and efficient nanocatalyst for oxidative desulphurization of gasoline. *RSC Adv.* **2016**, *6*, 53069–53079. [\[CrossRef\]](#)
- Hossain, M.N.; Park, H.C.; Choi, H.S. A comprehensive review on catalytic oxidative desulfurization of liquid fuel oil. *Catalysts* **2019**, *9*, 229. [\[CrossRef\]](#)
- Campos-Martin, J.M.; Capel-Sanchez, M.C. Catalytic oxidative desulfurization of liquid fuels. In *Catalytic and Noncatalytic Upgrading of Oils*; Dalai, A.K., Dadyburjor, D.B., Zheng, Y., Duan, A., Roberts, W.L., Nanda, S., Eds.; American Chemical Society: Washington, DC, USA, 2021; pp. 143–174.

22. Rajendran, A.; Cui, T.Y.; Fan, H.X.; Yang, Z.F.; Feng, J.; Li, W.Y. A comprehensive review on oxidative desulfurization catalysts targeting clean energy and environment. *J. Mater. Chem. A* **2020**, *8*, 2246–2285. [\[CrossRef\]](#)
23. Rezvani, M.A.; Khalafi, N. Synthesis of a new nanocomposite based on sandwich-type silicotungstate and polyvinyl alcohol with superior catalytic activity for deep desulfurization of real/thiophenic mode fuel. *J. Coord. Chem.* **2020**, *73*, 3395–3411. [\[CrossRef\]](#)
24. Maslova, O.; Senko, O.; Stepanov, N.; Gladchenko, M.; Gaydamaka, S.; Akopyan, A.; Polikarpova, P.; Lysenko, S.; Anisimov, A.; Efremenko, E. Formation and use of anaerobic consortia for the biotransformation of sulfur-containing extracts from pre-oxidized crude oil and oil fractions. *Bioresour. Technol.* **2021**, *319*, 124248. [\[CrossRef\]](#)
25. Rezvani, M.A.; Hadi, M.; Rezvani, H. Synthesis of new nanocomposite based on ceramic and heteropolymolybdate using leaf extract of *Aloe vera* as a high-performance nanocatalyst to desulfurization of real fuel. *Appl. Organomet. Chem.* **2021**, *35*, e6176. [\[CrossRef\]](#)
26. Rezvani, M.A.; Shaterian, M.; Shokri Aghbolagh, Z.; Babaei, R. Oxidative desulfurization of gasoline catalyzed by IMID@PMA@CS nanocomposite as a high-performance amphiphilic nanocatalyst. *Environ. Prog. Sustain. Energy* **2018**, *37*, 1891–1900. [\[CrossRef\]](#)
27. Rezvani, M.A.; Khandan, S.; Sabahi, N. Oxidative desulfurization of gas oil catalyzed by (TBA)4PW11Fe@PbO as an efficient and recoverable heterogeneous phase-transfer nanocatalyst. *Energy Fuels* **2017**, *31*, 5472–5481. [\[CrossRef\]](#)
28. Weh, R.; de Klerk, A. Thermochemistry of sulfones relevant to oxidative desulfurization. *Energy Fuels* **2017**, *31*, 6607–6614. [\[CrossRef\]](#)
29. Rankin, J.; Litz, K.; Briggs, S.; McCaskill, T.; Scudder, M.; Khalid, S.; Budhani, R. Selective desulfonylation of oxidized sulfur compounds in crude oil by alcohol-mediated nucleophilic attack studied by XANES and XRF spectroscopy. *Preprints* **2016**, 2016090075. [\[CrossRef\]](#)
30. Sundararaman, R.; Song, C. Oxidative desulfurization of crude oil incorporating sulfone decomposition by alkaline earth metal oxides. *Energy Fuels* **2013**, *27*, 6372–6376. [\[CrossRef\]](#)
31. Hansen, É.; Rodrigues, M.A.S.; Aragão, M.E.; de Aquim, P.M. Water and wastewater minimization in a petrochemical industry through mathematical programming. *J. Clean. Prod.* **2018**, *172*, 1814–1822. [\[CrossRef\]](#)
32. Ghimire, N.; Wang, S. Biological treatment of petrochemical wastewater. In *Petroleum Chemicals—Recent Insight*; Zoveidavianpoor, M., Ed.; IntechOpen: London, UK, 2018; pp. 55–74.
33. Ding, P.; Chu, L.; Wang, J. Advanced treatment of petrochemical wastewater by combined ozonation and biological aerated filter. *Environ. Sci. Pollut. Res.* **2018**, *25*, 9673–9682. [\[CrossRef\]](#)
34. Ahmadi, M.; Ahmadmoazzam, M.; Saeedi, R.; Abtahi, M.; Ghafari, S.; Jorfi, S. Biological treatment of a saline and recalcitrant petrochemical wastewater by using a newly isolated halo-tolerant bacterial consortium in MBBR. *Desalin. Water Treat.* **2019**, *167*, 84–95. [\[CrossRef\]](#)
35. Martínez, I.; Mohamed, M.E.S.; Santos, V.E.; García, J.L.; García-Ochoa, F.; Díaz, E. Metabolic and process engineering for biodesulfurization in Gram-negative bacteria. *J. Biotechnol.* **2017**, *262*, 47–55. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Sousa, J.M.; Ferreira, P.; Neves, R.P.; Ramos, M.J.J.; Fernandes, P.A. The bacterial 4S pathway—A benign and economic alternative for crude oil desulphurization. *Green Chem.* **2020**, *22*, 7604–7621. [\[CrossRef\]](#)
37. Sampanthar, J.T.; Xiao, H.; Dou, J.; Nah, T.Y.; Rong, X.; Kwan, W.P. A novel oxidative desulfurization process to remove refractory sulfur compounds from diesel fuel. *Appl. Catal. B* **2006**, *63*, 85–93. [\[CrossRef\]](#)
38. Kairbekov, Z.K.; Myltykbaeva, Z.K.; Mukhtaly, D.; Nysanova, B.; Anisimov, A.V.; Akopyan, A.V. Peroxide oxidative desulfurization of a diesel fuel. *Theor. Found. Chem. Eng.* **2018**, *52*, 677–680. [\[CrossRef\]](#)
39. Abro, R.; Abdeltawab, A.A.; Al-Deyab, S.S.; Yu, G.; Qazi, A.B.; Gao, S.; Chen, X. A review of extractive desulfurization of fuel oils using ionic liquids. *RSC Adv.* **2014**, *4*, 35302–35317. [\[CrossRef\]](#)
40. Julião, D.; Gomes, A.C.; Pillinger, M.; Valença, R.; Ribeiro, J.C.; Gonçalves, I.S.; Balula, S.S. Desulfurization of liquid fuels by extraction and sulfoxidation using H₂O₂ and [CpMo(CO)₃R] as catalysts. *Appl. Catal. B* **2018**, *230*, 177–183. [\[CrossRef\]](#)
41. Wang, D.H.; Qian, E.W.H.; Amano, H.; Okata, K.; Ishihara, A.; Kabe, T. Oxidative desulfurization of fuel oil: Part I. Oxidation of dibenzothiophenes using tert-butyl hydroperoxide. *Appl. Catal. A* **2003**, *253*, 91–99. [\[CrossRef\]](#)
42. Noyori, R. Pursuing practical elegance in chemical synthesis. *Chem. Comm.* **2005**, *14*, 1807–1811. [\[CrossRef\]](#)
43. Alheety, M.A.; Al-Jibori, S.A.; Karadağ, A.; Akbaş, H.; Ahmed, M.H. A novel synthesis of MnO₂ nanoflowers as an efficient heterogeneous catalyst for oxidative desulfurization of thiophenes. *Nano-Struct. Nano-Objects* **2019**, *20*, 100392. [\[CrossRef\]](#)
44. Anisimov, A.V.; Tarakanova, A.V. Oxidative desulfurization of hydrocarbon raw materials. *Russ. J. Gen.Chem.* **2009**, *79*, 1264–1273. [\[CrossRef\]](#)
45. Senko, O.; Maslova, O.; Gladchenko, M.; Gaydamaka, S.; Efremenko, E. Biogas production from biomass of microalgae *Chlorella vulgaris* in the presence of benzothiophene sulfone. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *525*, 012089.
46. Maslova, O.; Senko, O.; Stepanov, N.; Efremenko, E. Perspective approaches with the use of biocatalysts for improving the processes of polyaspartic acid production from oil benzene fraction after oxidative desulfurization. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *525*, 012037. [\[CrossRef\]](#)
47. Senko, O.; Maslova, O.; Gladchenko, M.; Gaydamaka, S.; Akopyan, A.; Lysenko, S.; Anisimov, A.; Efremenko, E. Prospective approach to the anaerobic bioconversion of benzo- and dibenzothiophene sulfones to sulfide. *Molecules* **2019**, *24*, 1736. [\[CrossRef\]](#)
48. Rezvani, M.A.; Aghbolagh, Z.S.; Monfared, H.H.; Khandan, S. Mono Mn(II)-substituted phosphotungstate@modified graphene oxide as a high-performance nanocatalyst for oxidative demercaptanization of gasoline. *J. Ind. Eng. Chem.* **2017**, *52*, 42–50. [\[CrossRef\]](#)

49. Rezvani, M.A.; Asli, M.A.; Khandan, S.; Mousavi, H.; Aghbolagh, Z.S. Synthesis and characterization of new nanocomposite CTAB-PTA@CS as an efficient heterogeneous catalyst for oxidative desulphurization of gasoline. *Chem. Eng. J.* **2017**, *312*, 243–251. [\[CrossRef\]](#)
50. Rezvani, M.A.; Khandan, S. Synthesis and characterization of a new nanocomposite (FeW11V@ CTAB-MMT) as an efficient heterogeneous catalyst for oxidative desulfurization of gasoline. *Appl. Organomet. Chem.* **2018**, *32*, e4524. [\[CrossRef\]](#)
51. Rezvani, M.A.; Maleki, Z. Facile synthesis of inorganic–organic $\text{Fe}_2\text{W}_{18}\text{Fe}_4\text{@NiO@CTS}$ hybrid nanocatalyst induced efficient performance in oxidative desulfurization of real fuel. *Appl. Organomet. Chem.* **2019**, *33*, e4895. [\[CrossRef\]](#)
52. Rezvani, M.A.; Fereyduni, M. Synthesis of organic–inorganic hybrid nanocomposite polyoxometalate/metal oxide/CS Polymer($\text{PMnW11@TiO}_2\text{@CS}$): Nanocatalyst for oxidative desulfurization of real fuel. *Chem. Sel.* **2019**, *4*, 11467–11474.
53. Rezvani, M.A.; Shaterian, M.; Khalafi, N. Synthesis and characterization of TBA-PV2Mo10@PVA as an efficient and reusable heterogeneous catalyst for oxidative desulfurization of gasoline. *J. Nanostruct.* **2019**, *9*, 349–364.
54. Rezvani, M.A.; Khandan, S. Synthesis and characterization of new sandwich-type polyoxometalate/nanoceramic nanocomposite, $\text{Fe}_2\text{W}_{18}\text{Fe}_4\text{@FeTiO}_3$, as a highly efficient heterogeneous nanocatalyst for desulfurization of fuel. *Solid State Sci.* **2019**, *98*, 106036. [\[CrossRef\]](#)
55. Rezvani, A.M.; Aghmasheh, M. Synthesis of a nanocomposite based on chitosan and modified heteropolyanion as a nanocatalyst for oxidative desulfurization of real and thiophenic model fuels. *J. Coord. Chem.* **2020**, *73*, 1407–1424. [\[CrossRef\]](#)
56. Rezvani, M.A.; Afshari, P.; Aghmasheh, M. Deep catalytic oxidative desulfurization process catalyzed by TBA-PWFe@NiO@BNT composite material as an efficient and recyclable phase-transfer nanocatalyst. *Mater. Chem. Phys.* **2021**, *267*, 124662. [\[CrossRef\]](#)
57. Rezvani, M.A.; Aghmasheh, M. Synthesis of t-B.PWFe/NiO nanocomposite as an efficient and heterogeneous green nanocatalyst for catalytic oxidative–extractive desulfurization of gasoline. *Environ. Prog. Sustain. Energy* **2021**, *40*, e13616. [\[CrossRef\]](#)
58. Rezvani, M.A.; Imani, A. Ultra-deep oxidative desulfurization of real fuels by sandwich-type polyoxometalate immobilized on copper ferrite nanoparticles, $\text{Fe}_6\text{W}_{18}\text{O}_{70}\text{@CuFe}_2\text{O}_4$, as an efficient heterogeneous nanocatalyst. *J. Environ. Chem. Eng.* **2021**, *9*, 105009. [\[CrossRef\]](#)
59. Alenazi, B.; Alsalmeh, A.; Alshammari, S.G.; Khan, R.; Siddiqui, M.R.H. Ionothermal synthesis of metal oxide-based nanocatalysts and their application towards the oxidative desulfurization of dibenzothiophene. *J. Chem.* **2020**, 3894804. [\[CrossRef\]](#)
60. Rezvani, M.A.; Hadi, M.; Mirsadri, S.A. Synthesis of new nanocomposite based on nanoceramic and mono substituted polyoxometalate, $\text{PMo}_{11}\text{Cd@MnFe}_2\text{O}_4$, with superior catalytic activity for oxidative desulfurization of real fuel. *Appl. Organomet. Chem.* **2020**, *34*, e5882. [\[CrossRef\]](#)
61. Rafiee, E.; Nobakht, N. Keggin type heteropoly acid, encapsulated in metal-organic framework: A heterogeneous and recyclable nanocatalyst for selective oxidation of sulfides and deep desulfurization of model fuels. *J. Mol. Catal. A Chem.* **2015**, *398*, 17–25. [\[CrossRef\]](#)
62. Banisharif, F.; Dehghani, M.R.; Capel-Sanchez, M.C.; Campos-Martin, J.M. Extractive-oxidative removals of dibenzothiophene and quinoline using vanadium substituted Dawson emulsion catalyst and ionic liquid based solvents. *J. Ind. Eng. Chem.* **2017**, *47*, 348–359. [\[CrossRef\]](#)
63. Ren, X.; Miao, G.; Xiao, Z.; Ye, F.; Li, Z.; Wang, H.; Xiao, J. Catalytic adsorptive desulfurization of model diesel fuel using $\text{TiO}_2\text{/SBA-15}$ under mild conditions. *Fuel* **2016**, *174*, 118–125. [\[CrossRef\]](#)
64. Julião, D.; Gomes, A.C.; Pillinger, M.; Cunha-Silva, L.; de Castro, B.; Gonçalves, I.S.; Balula, S.S. Desulfurization of model diesel by extraction/oxidation using a zinc-substituted polyoxometalate as catalyst under homogeneous and heterogeneous (MIL-101(Cr) encapsulated) conditions. *Fuel Process. Technol.* **2015**, *131*, 78–86. [\[CrossRef\]](#)
65. Kareem, Y.S.; Ammar, S.H.; Darwash, R.A. Microwave-induced catalytic oxidative desulfurization of gasoil fraction over phosphotungstic acid-based magnetic silica ($\text{Ni@SiO}_2\text{/PWA}$) nanocatalyst. *Catal. Commun.* **2020**, *136*, 105926. [\[CrossRef\]](#)
66. Zhang, Y.; Wang, R. Synthesis of silica@C-dots/phosphotung states core-shell microsphere for effective oxidative-adsorptive desulfurization of dibenzothiophene with less oxidant. *Appl. Catal. B Environ.* **2018**, *234*, 247–259. [\[CrossRef\]](#)
67. Venkateshwar, T.R.; Sain, B.; Kafola, S.; Sharma, Y.K.; Nanoti, S.M.; Garg, M.O. Oxidative desulfurization of HDS diesel using the aldehyde/molecular oxygen oxidation system. *Energy Fuels* **2007**, *21*, 3420–3424. [\[CrossRef\]](#)
68. Wang, J.; Zhao, D.; Li, K. Oxidative desulfurization of dibenzothiophene using ozone and hydrogen peroxide in ionic liquid. *Energy Fuels* **2010**, *24*, 2527–2534. [\[CrossRef\]](#)
69. Akopyan, A.; Polikarpova, P.; Gul, O.; Anisimov, A.; Karakhanov, E. Catalysts based on acidic SBA-15 for deep oxidative desulfurization of model fuels. *Energy Fuels* **2020**, *34*, 14611–14619. [\[CrossRef\]](#)
70. Kemei, M.C.; Barton, P.T.; Moffitt, S.L.; Gaultois, M.W.; Kurzman, J.A.; Seshadri, R.; Suchomer, M.R.; Kim, Y.I. Crystal structures of spin-Jahn–Teller-ordered MgCr_2O_4 and ZnCr_2O_4 . *J. Phys. Condens. Matter* **2013**, *25*, 326001. [\[CrossRef\]](#) [\[PubMed\]](#)
71. Kamel, L.; Anbia, M. Composite beads of molybdenum oxide supported on textured silicon as an oxidative desulfurization nanocatalyst. *Silicon* **2020**, *12*, 1325–1336. [\[CrossRef\]](#)
72. Hasannia, S.; Kazemeini, M.; Rashidi, A.; Seif, A. The oxidative desulfurization process performed upon a model fuel utilizing modified molybdenum based nanocatalysts: Experimental and density functional theory investigations under optimally prepared and operated conditions. *Appl. Surf. Sci.* **2020**, *527*, 146798. [\[CrossRef\]](#)
73. Ma, R.; Guo, J.; Wang, D.; He, M.; Xun, S.; Gu, J.; Zhu, W.; Li, H. Preparation of highly dispersed WO_3 /few layer $\text{g-C}_3\text{N}_4$ and its enhancement of catalytic oxidative desulfurization activity. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *572*, 250–258.

74. Li, X.; Yang, X.; Zhou, F.; Zhang, J.; Yang, H.; Wang, Y.; Zhao, Y.; Yuan, X.; Ju, J.; Hu, S. Construction of novel amphiphilic [Bmin]₃PMo₁₂O₄₀/g-C₃N₄ heterojunction catalyst with outstanding photocatalytic oxidative desulfurization performance under visible light. *J. Taiwan Inst. Chem. Eng.* **2019**, *100*, 210–219. [\[CrossRef\]](#)
75. Rafiee, E.; Khodayari, M. Synthesis and characterization of PMoV/Fe₃O₄/g-C₃N₄ from melamine: An industrial green nanocatalyst for deep oxidative desulfurization. *Chin. J. Catal.* **2017**, *38*, 458–468. [\[CrossRef\]](#)
76. Mahmoudabadi, Z.S.; Rashidi, A.; Yousefi, M. Synthesis of 2D-porous MoS₂ as a nanocatalyst for oxidative desulfurization of sour gas condensate: Process parameters optimization based on the Levenberg–Marquardt algorithm. *J. Environ. Chem. Eng.* **2021**, *9*, 105200. [\[CrossRef\]](#)
77. Karakhanov, E.; Akopyan, A.; Golubev, O.; Anisimov, A.; Glotov, A.; Vutolkina, A.; Maximov, A. Alkali earth catalysts based on mesoporous MCM-41 and Al-SBA-15 for sulfone removal from middle distillates. *ACS Omega* **2019**, *4*, 12736–12744. [\[CrossRef\]](#) [\[PubMed\]](#)
78. Akopyan, A.V.; Shlenova, A.O.; Cherednichenko, K.A.; Polikarpova, P.D. Immobilized multifunctional ionic liquids for highly efficient oxidation of sulfur-containing compounds in model fuels. *Energy Fuels* **2021**, *35*, 6755–6764. [\[CrossRef\]](#)
79. Rezvani, M.A.; Oveisi, M.; Asli, M.A.N. Phosphotungstovanadate immobilized on PVA as an efficient and reusable nano catalyst for oxidative desulphurization of gasoline. *J. Mol. Catal. A Chem.* **2015**, *410*, 121–132. [\[CrossRef\]](#)
80. Moeinifard, B.; Chermahini, A.N. Mono lacunary phosphomolybdate supported on mesoporous graphitic carbon nitride: An eco-friendly and efficient catalyst for oxidative desulfurization of the model and real fuels. *J. Environ. Chem. Eng.* **2021**, *9*, 105430. [\[CrossRef\]](#)
81. Chen, K.; Zhang, X.M.; Yang, X.F.; Jiao, M.G.; Zhou, Z.; Zhang, M.H.; Wang, D.X.; Bu, X.H. Electronic structure of heterojunction MoO₂/g-C₃N₄ catalyst for oxidative desulfurization. *Appl. Catal. B* **2018**, *238*, 263–273. [\[CrossRef\]](#)
82. Chen, M.L.; Zhou, S.Y.; Xu, Z.; Ding, L.; Cheng, Y.H. Metal-organic frameworks of MIL-100 (Fe, Cr) and MIL-101 (Cr) for aromatic amines adsorption from aqueous solutions. *Molecules* **2019**, *24*, 3718. [\[CrossRef\]](#) [\[PubMed\]](#)
83. Meman, N.M.; Zarenezhad, B.; Rashidi, A.; Hajjar, Z.; Esmaeili, E. Application of palladium supported on functionalized MWNTs for oxidative desulfurization of naphtha. *J. Ind. Eng. Chem.* **2015**, *22*, 179–184. [\[CrossRef\]](#)
84. Ahmad, W.; Ahmad, I. Mechanisms of desulfurization by nanomaterials. In *Nanotechnology in Oil and Gas Industries*; Saleh, T.A., Ed.; Springer: Cham, Switzerland, 2018; pp. 211–243.
85. Maciucă, A.L.; Ciocan, C.E.; Dumitriu, E.; Fajula, F.; Hulea, V. V-, Mo- and W-containing layered double hydroxides as effective catalysts for mild oxidation of thioethers and thiophenes with H₂O₂. *Catal. Today* **2008**, *138*, 33–37. [\[CrossRef\]](#)
86. Otsuki, S.; Nonaka, T.; Takashima, N.; Qian, W.; Ishihara, A.; Imai, T.; Kabe, T. Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction. *Energy Fuels* **2000**, *14*, 1232–1239. [\[CrossRef\]](#)
87. Pal, S.; Saha, B.; Sengupta, S. Oxidative desulphurization of model fuel by metal impregnated Ti-β catalysts. *Int. Res. J. Eng. Technol.* **2017**, *4*, 2376–2381.
88. Margeta, D.; Grčić, I.; Papić, S.; Sertić-Bionda, K.; Foglar, L. Impact of ultrasound application on oxidative desulphurization of diesel fuel and on treatment of resulting wastewater. *Environ. Technol.* **2016**, *37*, 293–299. [\[CrossRef\]](#)
89. Haruna, S.Y.; Faruq, U.; Zubairu, A.Y.; Liman, M.; Riskuwa, M.L. Comparative studies on reduction of sulphur content of heavy crude oil using KMnO₄ + H₂O₂/CH₃COOH and KMnO₄ + H₂O₂/HCOOH via oxidative desulphurization (ODS). *Am. J. Appl. Chem.* **2018**, *6*, 15–24. [\[CrossRef\]](#)
90. Dinamarca, M.A.; Ibacache-Quiroga, C.; Baeza, P.; Galvez, S.; Villarroel, M.; Olivero, P.; Ojeda, J. Biodesulfurization of gas oil using inorganic supports biomodified with metabolically active cells immobilized by adsorption. *Bioresour. Technol.* **2010**, *101*, 2375–2378. [\[CrossRef\]](#) [\[PubMed\]](#)
91. Zhang, Q.; Zhu, M.; Jones, I.; Zhang, Z.; Zhang, D. Desulfurization of spent tire pyrolysis oil and its distillate via combined catalytic oxidation using H₂O₂ with formic acid and selective adsorption over Al₂O₃. *Energy Fuels* **2020**, *34*, 6209–6219. [\[CrossRef\]](#)
92. Qiu, L.; Cheng, Y.; Yang, C.; Zeng, G.; Long, Z.; Wei, S.; Zhao, K.; Luo, L. Oxidative desulfurization of dibenzothiophene using a catalyst of molybdenum supported on modified medicinal stone. *RSC Adv.* **2016**, *6*, 17036–17045. [\[CrossRef\]](#)
93. Dehkordi, A.M.; Sobati, M.A.; Nazem, M.A. Oxidative desulfurization of non-hydrotreated kerosene using hydrogen peroxide and acetic acid. *Chin. J. Chem. Eng.* **2009**, *17*, 869–874. [\[CrossRef\]](#)
94. Al-Shafei, E.N.; Hamad, E.Z. Selective Liquid-Liquid Extraction of Oxidative Desulfurization Reaction Products. U.S. Patent No. 10,947,461B2, 16 March 2021.
95. Komintarachat, C.; Trakarnpruk, W. Oxidative desulfurization using polyoxometalates. *Ind. Eng. Chem. Res.* **2006**, *45*, 1853–1856. [\[CrossRef\]](#)
96. Choi, G.G.; Oh, S.J.; Kim, J.S. Clean pyrolysis oil from a continuous two-stage pyrolysis of scrap tires using in-situ and ex-situ desulfurization. *Energy* **2017**, *141*, 2234–2241. [\[CrossRef\]](#)
97. Ghahremani, H.; Nasri, Z.; Eikani, M.H. Ultrasound-assisted oxidative desulfurization (UAOD) of Iranian heavy crude oil: Investigation of process variables. *J. Pet. Sci. Eng.* **2021**, *204*, 108709. [\[CrossRef\]](#)
98. Akopyan, A.V.; Fedorov, R.A.; Andreev, B.V.; Tarakanova, A.V.; Anisimov, A.V.; Karakhanov, E.A. Oxidative desulfurization of hydrocarbon feedstock. *Russ. J. Appl. Chem.* **2018**, *91*, 529–542. [\[CrossRef\]](#)
99. Zeng, X.; Xiao, X.; Li, Y.; Chen, J.; Wang, H. Deep desulfurization of liquid fuels with molecular oxygen through graphene photocatalytic oxidation. *Appl. Catal. B Environ.* **2017**, *209*, 98–109. [\[CrossRef\]](#)

100. Lu, P.; Zhao, Y.; Dong, J.; Mei, B.B.; Du, X.L.; Jiang, Z.; Lui, Y.M.; He, H.Y.; Wang, Y.D.; Duan, X.Z.; et al. Direct and efficient synthesis of clean H_2O_2 from CO -assisted aqueous O_2 reduction. *ACS Catal.* **2020**, *10*, 13993–14005. [\[CrossRef\]](#)
101. Garrigues, L.; Maignien, L.; Lombard, E.; Singh, J.; Guillouet, S.E. Isopropanol production from carbon dioxide in *Cupriavidus necator* in a pressurized bioreactor. *New Biotechnol.* **2020**, *56*, 16–20. [\[CrossRef\]](#) [\[PubMed\]](#)
102. Ávila, M.; Rochón, E.; Lareo, C. Improvements in the formulation of sugarcane-sweet sorghum juices fermentation media for enhanced isopropanol and butanol production. *Biomass Conv. Bioref.* **2021**. [\[CrossRef\]](#)
103. Bulushev, D.A.; Ross, J.R. Towards sustainable production of formic acid. *Chem. Sustain. Chem.* **2018**, *11*, 821–836. [\[CrossRef\]](#)
104. Zhang, Z.; Liu, S.; Hou, M.; Yang, G.; Han, B. Continuous-flow formic acid production from the hydrogenation of CO_2 without any base. *Green Chem.* **2021**, *23*, 1978–1982. [\[CrossRef\]](#)
105. Vashisht, A.; Thakur, K.; Kauldhar, B.S.; Kumar, V.; Yadav, S.K. Waste valorization: Identification of an ethanol tolerant bacterium *Acetobacter pasteurianus* SKYAA25 for acetic acid production from apple pomace. *Sci. Total Environ.* **2019**, *690*, 956–964. [\[CrossRef\]](#)
106. Wu, Y.; Liu, X.; Wang, D.; Chen, Y.; Yang, Q.; Chen, Y.; Hu, X.; Xu, Q.; Fu, Q.; Du, C. Iron electrodes activating persulfate enhances acetic acid production from waste activated sludge. *Chem. Eng. J.* **2020**, *390*, 124580. [\[CrossRef\]](#)
107. Verbeeck, K.; Gildemyn, S.; Rabaey, K. Membrane electrolysis assisted gas fermentation for enhanced acetic acid production. *Front. Energy Res.* **2018**, *6*, 88. [\[CrossRef\]](#)
108. Fazzino, F.; Mauriello, F.; Paone, E.; Sidari, R.; Calabrò, P.S. Integral valorization of orange peel waste through optimized ensiling: Lactic acid and bioethanol production. *Chemosphere* **2021**, *271*, 129602. [\[CrossRef\]](#) [\[PubMed\]](#)
109. Yang, X.; Wang, S.; Li, G.; Zhao, F.; Feng, Z.; Chen, X.; Zhu, Z.; Wang, Y.; Gao, J. Process design and comprehensive analysis of the ethanol amination process to improve acetonitrile production. *Ind. Eng. Chem. Res.* **2020**, *59*, 5047–5055. [\[CrossRef\]](#)
110. Efremenko, E.N.; Stepanov, N.A.; Nikolskaya, A.B.; Senko, O.V.; Spiricheva, O.V.; Varfolomeev, S.D. Biocatalysts based on immobilized cells of microorganisms in the production of bioethanol and biobutanol. *Catal. Ind.* **2011**, *3*, 41–46. [\[CrossRef\]](#)
111. Lammens, T.M.; Gangarapu, S.; Franssen, M.C.; Scott, E.L.; Sanders, J.P. Techno-economic assessment of the production of bio-based chemicals from glutamic acid. *Biofuel. Bioprod. Biorefin.* **2012**, *6*, 177–187. [\[CrossRef\]](#)
112. Bi, Q.Y.; Lin, J.D.; Liu, Y.M.; Xie, S.H.; He, H.Y.; Cao, Y. Partially reduced iridium oxide clusters dispersed on titania as efficient catalysts for facile synthesis of dimethylformamide from CO_2 , H_2 and dimethylamine. *Chem. Commun.* **2014**, *50*, 9138–9140. [\[CrossRef\]](#)
113. Van Bennekom, J.G.; Venderbosch, R.H.; Assink, D.; Lemmens, K.P.J.; Heeres, H.J. Bench scale demonstration of the Supermethanol concept: The synthesis of methanol from glycerol derived syngas. *Chem. Eng. J.* **2012**, *207*, 245–253. [\[CrossRef\]](#)
114. Atlas, R.M. *Handbook of Microbiological Media*; CRC Press: Boca Raton, FL, USA, 2010; 2040p.
115. Yokoi, H.; Hirose, M.S.; Hayashi, S. Microbial production of hydrogen from starch-manufacturing wastes. *Biomass Bioenerg.* **2002**, *22*, 389–395. [\[CrossRef\]](#)
116. Somerville, H.J.; Mason, J.R.; Ruffell, R.N. Benzene degradation by bacterial cells immobilized in polyacrylamide gel. *Eur. J. Appl. Microbiol. Biotechnol.* **1977**, *4*, 75–85. [\[CrossRef\]](#)
117. Hallaji, S.M.; Siami, S.; Aminzadeh, B. Improvement of anaerobic digestion of sewage sludge, using combined hydrogen peroxide and thermal pre-treatment. *Pollution* **2019**, *5*, 487–499.
118. Ambrose, H.W.; Philip, L.; Suraishkumar, G.K.; Karthikaichamy, A.; Sen, T.K. Anaerobic co-digestion of activated sludge and fruit and vegetable waste: Evaluation of mixing ratio and impact of hybrid (microwave and hydrogen peroxide) sludge pre-treatment on two-stage digester stability and biogas yield. *J. Water Process. Eng.* **2020**, *37*, 101498. [\[CrossRef\]](#)
119. Song, Z.L.; Yag, G.H.; Feng, Y.Z.; Ren, G.X.; Han, X.H. Pretreatment of rice straw by hydrogen peroxide for enhanced methane yield. *J. Integr. Agric.* **2013**, *12*, 1258–1266. [\[CrossRef\]](#)
120. Ksibi, M. Chemical oxidation with hydrogen peroxide for domestic wastewater treatment. *Chem. Eng. J.* **2006**, *119*, 161–165. [\[CrossRef\]](#)
121. Park, E.S. Mechanical properties and antibacterial activity of peroxide-cured silicone rubber foams. *J. Appl. Polym. Sci.* **2008**, *110*, 1723–1729. [\[CrossRef\]](#)
122. Mei, X.; Ding, Y.; Li, P.; Xu, L.; Wang, Y.; Guo, Z.; Shen, W.; Yang, Y.; Wang, Y.; Xiao, Y.; et al. A novel system for zero-discharge treatment of high-salinity acetonitrile-containing wastewater: Combination of pervaporation with a membrane-aerated bioreactor. *Chem. Eng. J.* **2020**, *384*, 123338. [\[CrossRef\]](#)
123. Kong, Z.; Li, L.; Kurihara, R.; Kubota, K.; Li, Y.Y. Anaerobic treatment of N, N-dimethylformamide-containing wastewater by co-culturing two sources of inoculum. *Water Res.* **2018**, *139*, 228–239. [\[CrossRef\]](#)
124. Kong, Z.; Li, L.; Wu, J.; Zhang, T.; Li, Y.Y. Insights into the methanogenic degradation of N,N-dimethylformamide: The functional microorganisms and their ecological relationships. *Bioresour. Technol.* **2019**, *271*, 37–47. [\[CrossRef\]](#)
125. Wang, J.; Liu, X.; Jiang, X.; Zhang, L.; Hou, C.; Su, G.; Wang, L.; Mu, Y.; Shen, J. Nitrate stimulation of N-Methylpyrrolidone biodegradation by *Paracoccus pantotrophus*: Metabolite mechanism and genomic characterization. *Bioresour. Technol.* **2019**, *294*, 122185. [\[CrossRef\]](#)
126. Senko, O.; Gladchenko, M.; Maslova, O.; Efremenko, E. Long-term storage and use of artificially immobilized anaerobic sludge as a powerful biocatalyst for conversion of various wastes including those containing xenobiotics to biogas. *Catalysts* **2019**, *9*, 326. [\[CrossRef\]](#)
127. Malani, R.S.; Batghare, A.H.; Bhasarkar, J.B.; Moholkar, V.S. Kinetic modeling and process engineering aspects of biodesulfurization of liquid fuels: Review and analysis. *Bioresour. Technol. Rep.* **2021**, *14*, 100668. [\[CrossRef\]](#)

128. Lateef, S.A.; Ajumobi, O.O.; Onaizi, S.A. Enzymatic desulfurization of crude oil and its fractions: A mini review on the recent progresses and challenges. *Arab. J. Sci. Eng.* **2019**, *44*, 5181–5193. [\[CrossRef\]](#)
129. Bachmann, R.T.; Johnson, A.C.; Edyvean, R.G. Biotechnology in the petroleum industry: An overview. *Int. Biodeterior. Biodegrad.* **2014**, *86*, 225–237. [\[CrossRef\]](#)
130. Rossi, G. The microbial desulfurization of coal. In *Geobiotechnology II*; Schippers, A., Glombitza, F., Sand, W., Eds.; Springer: Berlin/Heidelberg, Germany, 2013; pp. 147–167.
131. Fenibo, E.O.; Ijoma, G.N.; Selvarajan, R.; Chikere, C.B. Microbial surfactants: The next generation multifunctional biomolecules for applications in the petroleum industry and its associated environmental remediation. *Microorganisms* **2019**, *7*, 581. [\[CrossRef\]](#) [\[PubMed\]](#)
132. Sohrabi, M.; Kamyab, H.; Janalizadeh, N.; Huyop, F.Z. Bacterial desulfurization of organic sulfur compounds exist in fossil fuels. *J. Pure Appl. Microbiol.* **2012**, *6*, 717–729.
133. Gupta, N.; Roychoudhury, P.K.; Deb, J.K. Biotechnology of desulfurization of diesel: Prospects and challenges. *Appl. Microbiol. Biotechnol.* **2005**, *66*, 356–366. [\[CrossRef\]](#)
134. Martínez, I.; Mohamed, M.E.S.; Rozas, D.; García, J.L.; Díaz, E. Engineering synthetic bacterial consortia for enhanced desulfurization and revalorization of oil sulfur compounds. *Metab. Eng.* **2016**, *35*, 46–54. [\[CrossRef\]](#)
135. Nuhu, A.A. Bio-catalytic desulfurization of fossil fuels: A mini review. *Rev. Environ. Sci. Biotechnol.* **2013**, *12*, 9–23. [\[CrossRef\]](#)
136. Xu, P.; Feng, J.; Yu, B.; Li, F.; Ma, C. Recent developments in biodesulfurization of fossil fuels. *Adv. Biochem Eng Biotechnol.* **2009**, *113*, 255–274.
137. Gallagher, J.R.; Olson, E.S.; Stanley, D.C. Microbial desulfurization of dibenzothiophene: A sulfur-specific pathway. *FEMS Microbiol. Lett.* **1993**, *107*, 31–35. [\[CrossRef\]](#)
138. Aggarwal, S.; Karimi, I.A.; Kilbane, J.J., II; Lee, D.Y. Roles of sulfite oxidoreductase and sulfite reductase in improving desulfurization by *Rhodococcus erythropolis*. *Mol. Biosys.* **2012**, *8*, 2724–2732. [\[CrossRef\]](#) [\[PubMed\]](#)
139. Gray, K.A.; Pogrebinsky, O.S.; Mrachko, G.T.; Xi, L.; Monticello, D.J.; Squires, C.H. Molecular mechanisms of biocatalytic desulfurization of fossil fuels. *Nat. Biotechnol.* **1996**, *14*, 1705–1709. [\[CrossRef\]](#)
140. Javadli, R.; De Klerk, A. Desulfurization of heavy oil. *Appl. Petrochem. Res.* **2012**, *1*, 3–19. [\[CrossRef\]](#)
141. Li, X.; Chen, S.; Dong, B.; Dai, X. New insight into the effect of thermal hydrolysis on high solid sludge anaerobic digestion: Conversion pathway of volatile sulphur compounds. *Chemosphere* **2020**, *244*, 125466. [\[CrossRef\]](#) [\[PubMed\]](#)
142. Kurita, S.; Endo, T.; Nakamura, H.; Yagi, T.; Tamiya, N. Decomposition of some organic sulfur compounds in petroleum by anaerobic bacteria. *J. Gen. Appl. Microbiol.* **1971**, *17*, 185–198. [\[CrossRef\]](#)
143. Kim, B.H.; Kim, H.Y.; Kim, T.S.; Park, D.H. Selectivity of desulfurization activity of *Desulfovibrio desulfuricans* M6 on different petroleum products. *Fuel Process. Technol.* **1995**, *43*, 87–94. [\[CrossRef\]](#)
144. Efremenko, E.N. *Immobilized Cells: Biocatalysts and Processes*; RIOR: Moscow, Russia, 2018; 500p.
145. Maslova, O.V.; Senko, O.V.; Stepanov, N.A.; Efremenko, E.N. Lactic acid production using free cells of bacteria and filamentous fungi and cells immobilized in polyvinyl alcohol cryogel: A comparative analysis of the characteristics of biocatalysts and processes. *Catal. Ind.* **2016**, *8*, 280–285. [\[CrossRef\]](#)
146. Lalov, I.G.; Krysteva, M.A.; Phelouzat, J.L. Improvement of biogas production from vinasse via covalently immobilized methanogens. *Bioresour. Technol.* **2001**, *79*, 83–85. [\[CrossRef\]](#)
147. Chauhan, A.; Ogram, A. Evaluation of support matrices for immobilization of anaerobic consortia for efficient carbon cycling in waste regeneration. *Biochem. Biophys. Res. Commun.* **2005**, *327*, 884–893. [\[CrossRef\]](#)
148. Naito, M.; Kawamoto, T.; Fujino, K.; Kobayashi, M.; Maruhashi, K.; Tanaka, A. Long-term repeated biodesulfurization by immobilized *Rhodococcus erythropolis* KA2-5-1 cells. *Appl. Microbiol. Biotechnol.* **2001**, *55*, 374–378. [\[CrossRef\]](#)
149. Li, Y.G.; Gao, H.S.; Li, W.L.; Xing, J.M.; Liu, H.Z. *In situ* magnetic separation and immobilization of dibenzothiophene-desulfurizing bacteria. *Bioresour. Technol.* **2009**, *100*, 5092–5096. [\[CrossRef\]](#) [\[PubMed\]](#)
150. Chang, J.H.; Rhee, S.K.; Chang, Y.K.; Chang, H.N. Desulfurization of diesel oils by a newly isolated dibenzothiophene-degrading *Nocardia* sp. strain CYKS2. *Biotechnol. Prog.* **1998**, *14*, 851–855. [\[CrossRef\]](#) [\[PubMed\]](#)
151. Peng, Y.; Wen, J. Modeling of DBT biodesulfurization by resting cells of *Gordonia* sp. WQ-01A immobilized in alginate gel beads in an oil-water-immobilization system. *Chem. Biochem. Eng. Q* **2010**, *24*, 85–94.
152. Li, Y.G.; Xing, J.M.; Xiong, X.C.; Li, W.L.; Gao, H.S.; Liu, H.Z. Improvement of biodesulfurization activity of alginate immobilized cells in biphasic systems. *J. Ind. Microbiol. Biotechnol.* **2008**, *35*, 145–150. [\[CrossRef\]](#) [\[PubMed\]](#)
153. Hou, Y.; Kong, Y.; Yang, J.; Zhang, J.; Shi, D.; Xin, W. Biodesulfurization of dibenzothiophene by immobilized cells of *Pseudomonas stutzeri* UP-1. *Fuel* **2005**, *84*, 1975–1979. [\[CrossRef\]](#)
154. Gunam, I.B.W.; Sitepu, A.; Antara, N.S.; Triani, I.G.A.L.; Arnata, I.W.; Setiyo, Y. Bacterial desulfurization of dibenzothiophene by *Pseudomonas* sp. strain KWN5 immobilized in alginate beads. *J. Teknol.* **2021**, *83*, 107–115. [\[CrossRef\]](#)
155. Chiroma, T.M.; Kareem, S.A.; Hayatuddeen, A.; Sokwa, T. Kinetics of biodesulfurization of diesel using immobilized cells. *Niger. J. Eng. Sci. Technol. Res.* **2020**, *6*, 6–12.
156. Dinamarca, M.A.; Rojas, A.; Baeza, P.; Espinoza, G.; Ibacache-Quiroga, C.; Ojeda, J. Optimizing the biodesulfurization of gas oil by adding surfactants to immobilized cell systems. *Fuel* **2014**, *116*, 237–241. [\[CrossRef\]](#)
157. Zhang, H.; Shan, G.; Liu, H.; Xing, J. Surface modification of γ -Al₂O₃ nano-particles with gum arabic and its applications in adsorption and biodesulfurization. *Surf. Coat. Technol.* **2007**, *201*, 6917–6921. [\[CrossRef\]](#)

158. Chang, J.H.; Chang, Y.K.; Ryu, H.W.; Chang, H.N. Desulfurization of light gas oil in immobilized-cell systems of *Gordona sp.* CYKS1 and *Nocardia sp.* CYKS2. *FEMS Microbiol. Lett.* **2000**, *182*, 309–312. [\[CrossRef\]](#)
159. Gunam, I.B.; Yamamura, K.; Sujaya, I.N.; Antara, N.S.; Aryanta, W.R.; Tanaka, M.; Tomiko, F.; Sone, T.; Asano, K. Biodesulfurization of dibenzothiophene and its derivatives using resting and immobilized cells of *Sphingomonas subarctica* T7b. *J. Microbiol. Biotechnol.* **2013**, *23*, 473–482. [\[CrossRef\]](#)
160. Dinamarca, M.A.; Orellana, L.; Aguirre, J.; Baeza, P.; Espinoza, G.; Canales, C.; Ojeda, J. Biodesulfurization of dibenzothiophene and gas oil using a bioreactor containing a catalytic bed with *Rhodococcus rhodochrous* immobilized on silica. *Biotechnol. Lett.* **2014**, *36*, 1649–1652. [\[CrossRef\]](#)
161. Maslova, O.V.; Senko, O.V.; Efremenko, E.N. Aspartic and glutamic acids polymers: Preparation and applications in medicinal chemistry and pharmaceuticals. *Russ. Chem. Bull.* **2018**, *67*, 614–623. [\[CrossRef\]](#)
162. Shan, G.B.; Xing, J.M.; Luo, M.F.; Liu, H.Z.; Chen, J.Y. Immobilization of *Pseudomonas delafieldii* with magnetic polyvinyl alcohol beads and its application in biodesulfurization. *Biotechnol. Lett.* **2003**, *25*, 1977–1981. [\[CrossRef\]](#)
163. Guobin, S.; Jianmin, X.; Chen, G.; Huizhou, L.; Jiayong, C. Biodesulfurization using *Pseudomonas delafieldii* in magnetic polyvinyl alcohol beads. *Let. Appl. Microbiol.* **2005**, *40*, 30–36.
164. Dai, Y.; Shao, R.; Qi, G.; Ding, B.B. Enhanced dibenzothiophene biodesulfurization by immobilized cells of *Brevibacterium lutescens* in n-octane–water biphasic system. *Appl. Biochem. Biotechnol.* **2014**, *174*, 2236–2244.
165. Humphries, A.C.; Nott, K.P.; Hall, L.D.; Macaskie, L.E. Reduction of Cr(VI) by immobilized cells of *Desulfovibrio vulgaris* NCIMB 8303 and *Microbacterium sp.* NCIMB 13776. *Biotechnol. Bioeng.* **2005**, *90*, 589–596. [\[CrossRef\]](#)
166. Worthington, M.J.; Kucera, R.L.; Chalker, J.M. Green chemistry and polymers made from sulfur. *Green Chem.* **2017**, *19*, 2748–2761. [\[CrossRef\]](#)
167. Kalyuzhnyi, S.; Gladchenko, M.; Mulder, A.; Versprille, B. Comparison of quasisteady-state performance of the DEAMOX process under intermittent and continuous feeding and different nitrogen loading rates. *Biotechnol.* **2007**, *2*, 894–900. [\[CrossRef\]](#)
168. Kalyuzhnyi, S.; Gladchenko, M.; Mulder, A.; Versprille, B. DEAMOX—New biological nitrogen removal process based on anaerobic ammonia oxidation coupled to sulphide-driven conversion of nitrate into nitrite. *Water Res.* **2006**, *40*, 3637–3645. [\[CrossRef\]](#) [\[PubMed\]](#)
169. Kalyuzhnyi, S.V.; Gladchenko, M.A.; Kang, H.; Mulder, A.; Versprille, A. Development and optimisation of VFA driven DEAMOX process for treatment of strong nitrogenous anaerobic effluents. *Water Sci. Technol.* **2008**, *57*, 323–328. [\[CrossRef\]](#)
170. Majolagbe, O.N.; Oloke, J.K.; Adegunlola, G.A.; Adebayo, E.A.; Oyeyiola, A.G.; Ola, I.O. Biodesulphurization of crude-oil using immobilized spores of *Rhizopus nigricans*. *Adv. Nat. Appl. Sci.* **2010**, *4*, 29–33.
171. Efremenko, E.N.; Maslova, O.V.; Kholstov, A.V.; Senko, O.V.; Ismailov, A.D. Biosensitive element in the form of immobilized luminescent photobacteria for detecting ecotoxins in aqueous flow-through systems. *Luminescence* **2016**, *31*, 1283–1289. [\[CrossRef\]](#)
172. Senko, O.; Stepanov, N.; Maslova, O.; Akhundov, R.; Ismailov, A.; Efremenko, E. Immobilized luminescent bacteria for the detection of mycotoxins under discrete and flow-through conditions. *Biosensors* **2019**, *9*, 63. [\[CrossRef\]](#)
173. Senko, O.V.; Maslova, O.V.; Efremenko, E.N. Optimization potential of anaerobic biocatalytic processes using intracellular ATP concentration as the main criterion for decision making. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *848*, 012080. [\[CrossRef\]](#)
174. Efremenko, E.; Maslova, O.; Stepanov, N.; Ismailov, A. Using cholinesterases and immobilized luminescent photobacteria for the express-analysis of mycotoxins and estimating the efficiency of their enzymatic hydrolysis. *Toxins* **2021**, *13*, 34. [\[CrossRef\]](#)
175. Maslova, O.; Stepanov, N.; Senko, O.; Efremenko, E. Production of various organic acids from different renewable sources by immobilized cells in the regimes of separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF). *Bioresour. Technol.* **2019**, *272*, 1–9. [\[CrossRef\]](#)
176. Bhasarkar, J.B.; Dikshit, P.K.; Moholkar, V.S. Ultrasound assisted biodesulfurization of liquid fuel using free and immobilized cells of *Rhodococcus rhodochrous* MTCC 3552: A mechanistic investigation. *Bioresour. Technol.* **2015**, *187*, 369–378. [\[CrossRef\]](#)
177. Derikvand, P.; Etemadifar, Z. Improvement of biodesulfurization rate of alginate immobilized *Rhodococcus erythropolis* R1. *Jundishapur J. Microbiol.* **2014**, *7*, e9123. [\[CrossRef\]](#)
178. Yu, B.; Shan, A.; Zhang, D.; Lou, Z.; Yuan, H.; Huang, X.; Zhu, N.; Hu, X. Dosing time of ferric chloride to disinhibit the excessive volatile fatty acids in sludge thermophilic anaerobic digestion system. *Bioresour. Technol.* **2015**, *189*, 154–161. [\[CrossRef\]](#) [\[PubMed\]](#)
179. Intanoo, P.; Rangsanvigat, P.; Malakul, P.; Chavadej, S. Optimization of separate hydrogen and methane production from cassava wastewater using two-stage upflow anaerobic sludge blanket reactor (UASB) system under thermophilic operation. *Bioresour. Technol.* **2014**, *173*, 256–265. [\[CrossRef\]](#)