Review

Advanced Technologies Conciliating Desulfurization and Denitrogenation to Prepare Clean Fuels

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Abstract: The removal of sulfur- and nitrogen-containing compounds present in fuels is and will be crucial to accomplish actual strict regulations to avoid environmental and humanity health adversities. The conventional hydrodesulfurization and hydrodenitrogenation processes conducted by refineries are limited due to severe operating conditions, and even more importantly, they are inefficient for simultaneously removing nitrogen- and sulfur-containing compounds in fuels. On the other hand, non-hydrogen technologies are beneficial in terms of mild operating conditions, and during the last two decades, some successful works have shown that these can be highly effective at efficiently removing both sulfur- and nitrogen-containing compounds from liquid fuels. For more than four decades, extensive research (thousands of publications since the 1980s) has been dedicated to developing remote desulfurization technologies without taking into consideration the presence of a complex fuel matrix, or even taking into account the presence of other harmful pollutant elements, such as nitrogen. Even more recently, several effective non-hydrogen denitrogenation processes have been reported without considering the presence of sulfur compounds. This review paper is a reflection on the limited work that has been successfully performed to simultaneously remove sulfur- and nitrogen-containing compounds from fuels. An evaluation of different methodologies (adsorption, extraction, oxidative (photo)catalysis, ultrasound-assisted oxidation) is presented here. Furthermore, this review intends to define new future strategies that will allow the design of more suitable and economical technologies, effectively conciliating desulfurization and denitrogenation processes to produce more sustainable fuels.

Keywords: denitrogenation; desulfurization; fuels; acid rains; oxidation; extraction; adsorption; catalyst; fuel

1. Introduction

Fossil fuels remain the main natural resource available to supply the enormous energy needs of current society. Furthermore, it is expected to comprise an impressive increment of energy consumption until 2040, associated with the expansion of the planet's population by 1.7 billion, while it is anticipated that renewable energy will only have a 20% higher contribution than the actual by 2040 [1]. This scenario predicts that largely fossil fuels will be used to satisfy the lion's share of global energy demand in the years ahead [2]. Fossil fuel usage compromises the health of our planet and humanity via pollution and large toxic gas emissions [3]. Heavy crude and fuel oils produced from unconventional sources are rich in sulfur- and nitrogen-containing compounds (SCCs and NCCs). Conventional crude oil produced from unconventional sources like oil shale, oil sand, vacuum residue, and coal are rich in SCCs and NCCs [4], whose removal demands immediate attention.

Both sulfur and nitrogen have deleterious impacts on the environment as well as human health, and thus, limitations are imposed on their maximum permissible limits [5–7]. These are responsible for the acid rains that are associated with major nefarious health, cultural heritage, and environmental effects, further contributing to escalating climate instability. The refining industry has made an effort to remove nitrogen and sulfur compounds from crude oil, mainly to improve the adverse effects on the quality of the refined products and the negative environmental impact [8]. The presence of nitrogen compounds in crude oil reduces the efficiency of the industrial process of hydrodesulfurization (HDS) via competitive adsorption of the catalyst. NCCs can poison the catalytic converters, reducing fuel economy, and even acidify lubricating oils [9,10]. During the last decade, the use of biofuels has increased to diminish the use of fossil fuels, mainly in the transportation sector. Biofuels are produced from biological sources and considered to be cleaner and greener fuel. Their sulfur content is low, but the amount of NCCs which must be removed to promote biofuel commercialization is considerably high (12.4% in terms of relative % C content) [11,12]. The removal of SCCs and NCCs from fuel oils is essential for bettering the environment, our assets, human health, and refinery process development. Various studies on separately removing NCCs or SSCs from fuel oils can be found in the literature, with reasonable removal efficiency (Figure 1). Many reviews on sole desulfurization [13–21] or denitrogenation [22–26] are available in the published literature. However, researchers are now focusing on simultaneous desulfurization and denitrogenation of fuel oils to achieve Environmental Protection Agency (EPA) requirements [27], but there is still scarce information regarding this area (Figure 1) [28–31]. This is because most technologies cannot carry out an effective simultaneous removal of nitrides and sulfides due to problems associated with technical or economic implementation. Exploring effective technologies for deep desulfurization with simultaneous denitrogenation is an attractive topic in producing clean fuels.
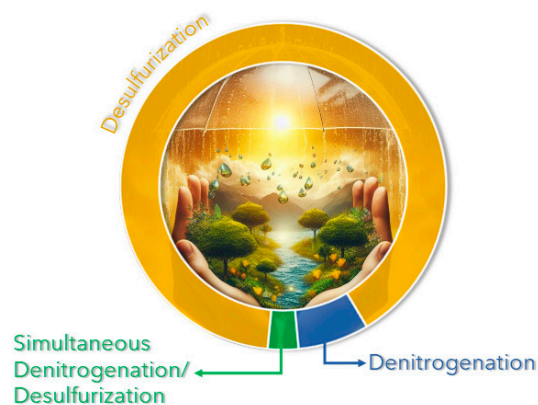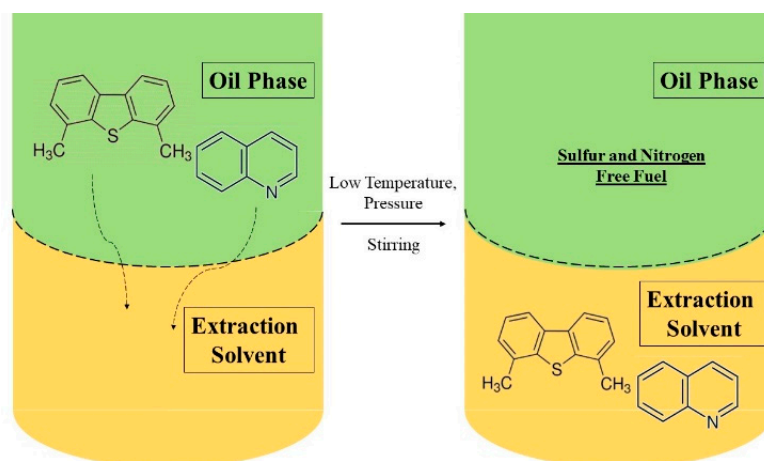

Figure 1. Schematic representation of the volume of isolated and simultaneous desulfurization and denitrogenation reported studies.

This review intends to elucidate the several technologies already reported, operating for simultaneous NCC and SCC compounds in model and real fuels. The works reported until now will be appointed to different technological sections: adsorption, extraction, oxidative (photo)catalysis, and ultrasound-assisted oxidation. The efficiency of the various technologies is compared, forming a crucial base of knowledge to develop more effective methodologies for simultaneously and highly efficiently removing sulfur and nitrogen from fuels.

2. Extractive Process

Extractive desulfurization (EDS) and extractive denitrogenation (EDN) are energetically sustainable, cost-effective methods to produce low-sulfur and nitrogen fuels. These techniques can be performed simultaneously (EDS/N) and do not require the utilization of

hydrogen or catalysts, as well as operating under simple conditions of low temperature and pressure [32,33]. Furthermore, these techniques are not destructive methods and thus do not have any impact on the quality of liquid fuels or on the chemical structure of the extracted valuable S- and N-compounds, which can be further processed into value-added products [34]. EDS and EDN are performed through a simple liquid–liquid extraction where the feedstock is mixed with an appropriate immiscible solvent in a biphasic system. S- and N-containing compounds present in the fuel oil are transferred to the appropriate solvent and separated by taking advantage of their nucleophilic properties and polarity (Figure 2).


Figure 2. Schematic representation of the extractive process of a biphasic system of a fuel oil containing S and N compounds and an extraction solvent.

After the adequate extraction time (frequently only a few minutes, 10–30 min.), the immiscible extraction solvent is easily separated from the fuel oil, and the organosulfur and nitrogen compounds are then removed to recover the extraction solvent via distillation. Further, this can be recycled to perform multiple extraction cycles [32]. The choice of an adequate extraction solvent plays a crucial role in the efficiency of this method. Desirable properties for an effective solvent for simultaneous EDS/N must comprise a high partition coefficient for sulfur and/or nitrogen compounds, negligible solubility in fuels, high thermal and chemical stabilities, nontoxicity, and low costs.

2.1. Ionic Liquids

Ionic liquids (ILs) as extraction solvents are attracting the most attention in desulfurization literature, but also in EDS/N [35]. Several reviews of extractive desulfurization and extractive denitrogenation have been written [22,30,36]; however, a gap of information is found in the literature, conciliating both EDS/N processes. ILs comprise organic cations and either organic or inorganic anions (Figure 3) with 10^{18} possible combinations, granting them designations such as "task specific" or "designer solvents", as their physicochemical properties can be tailored to specific applications [30].

The use of ILs as extraction solvents for fuel desulfurization and denitrogenation comes from their generally negligible vapor pressure, which allows the extracted product to be further separated from the ILs. Several studies using ILs for simultaneous desulfurization and denitrogenation have been conducted, allowing researchers to establish key factors in their design. ILs should be completely insoluble in oil, very selective towards S- and N-compounds (avoiding harming the other properties of fuels), affordable, easy to regenerate, and thermally and chemically stable.
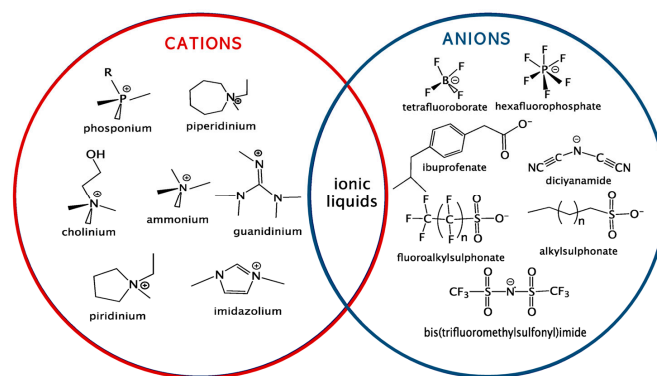
Figure 3. Representation of some of the most representative cations and anions present in ILs.

The pioneer study on the use of ILs for EDS/N of fuels reported different types of ILs, 1-alkyl-3-methylimidazolium (AMIM) tetrafluoroborate, hexafluorophosphate, and trimethylamine hydrochloride (AlCl$_3$-TMAC) with potential to be applied for sulfur removal in transportation fuels [33]. At low concentrations, S- and N-compounds were successfully removed from the fuel oil without competing, while N-compounds, such as pyridine and 2-methylpyridine, were miscible with the IL BMIMPF$_6$ (BMIM means 1-Butyl-3-methylimidazolium). However, at higher concentrations, it was found that performing N and S extraction was more difficult, although aromatic N-compound absorption was favored compared to S-compound extraction.

Hansmeier et al. studied pyridinium-based ILs as well as imidazolium-based ILs, and the two types of ILs were able to extract S- and N-containing heteroatoms from fuel oil systems [37]. ILs showed up to 50% more efficiency than other organic extraction solvents. In this work, it was possible to see that N-compounds were extracted more easily than S-compounds. Furthermore, it was also verified that for ILs to perform extractive processes, it was more important to have a higher capacity than a higher selectivity [38].

Chen et al. studied the extraction properties of Lewis acidic ILs 1-butyl-3-methylilimadazolium chloride/ZnCl$_2$ and [BMIM]ZnCl$_2$, as well as Brønsted acidic ILs [BMIM]HSO$_4$ and [HMIM]SO$_4$ (HMIM means 1-Hexyl-3-methylimidazolium) [32]. It was shown that [BMIM]ZnCl$_2$ had better results, obtaining 93.8% of both thiophene and carbazole removal. Chen et al. also studied temperature influence on the extractive process and concluded that it did not play an important role on the efficacy of the IL. It was also shown in this work that reducing the mass ratio between IL and oil did not affect N-compound removal but significantly decreased sulfur removal.

ILs present a higher extractive performance compared with other organic solvents; however, these can also be toxic, corrosive, and explosive. Further, IL synthesis is also far from being environmentally friendly, since it generally requires a large quantity of salts and solvents to achieve complete anion exchange, which also turns the price of these solvents extremely high [39–42].

Ongoing development of novel ILs with different constituents provides an opportunity for researchers to extend the application of these solvents; however, their undesirable aspects have led to the development of a selection for a new generation: low-cost ILs of facile preparation, deep eutectic solvents (DESs).

2.2. Deep Eutectic Solvents

DESs are a new generation of potential sustainable solvents, resulting from the eutectic mixture of green, easily available, and cheap raw components, capable of self-association [43]. These solvents exhibit physicochemical properties that are similar to those of traditionally used ILs while being inexpensive and environmentally friendly, as their preparation does not require expensive organic solvents. DESs have been applied in organic synthesis, electrochemistry, materials science, and catalysis [44–47]. Used in EDS/N, DESs should exhibit the same desirable properties as those expected for ILs. DESs should selectively remove sulfur and nitrogen compounds while avoiding co-extraction

of other aromatic species from fuel oil and exhibit low miscibility with alkyl chains in fuel, reducing cross-contamination. To ensure optimal efficiency, DESs should keep their viscosity at a minimum, promoting efficient mass transfer of sulfur species between the two phases.

The first reported work about the extraction of S- and N-containing compounds from mixtures with n-heptane using tetrahexylammonium bromide-based DES solvents was performed by Alli and Kroon [48]. The S- and N-containing compounds separated from the raffinate phase were benzothiazole and thiophene. Through selectivity and distribution coefficient studies, it was possible to achieve benzothiazole with a greater affinity in comparison to thiophene. Lima et al., studied the capacity to remove S- and N-compounds from the fuel oil of four other different DESs by combining one ammonium- or phosphonium-based salt with one complexing agent (PEG400 and Sulfolane) [49]. It was shown that in simultaneous EDS/N, the removal of N-compounds was favored by the presence of concurrent S-compounds, and it was possible to achieve the same level of extractive desulfurization as a single EDS process. Moreover, reusability studies showed that DESs suffer a significant reduction in the efficiency of extraction for S-compounds but not for N-compounds. This setback was completely overcome after a regeneration process where the performance of DESs was fully restored [26].

The ability of DESs to perform simultaneous EDS/N from real fuel was studied by Warrag et al. using a phosphonium-based DES of methyl triphenylphosphonium bromide and triethylene glycol [50]. After nine cycles of extraction, it was possible to remove all the S- and N-compounds from the fuel oil, with each cycle being performed at 298 K for 1 h. While the quinoline (QUI) was removed after only two extraction cycles, the thiophene required more cycles. Lemaoui et al. also studied simultaneous desulfurization and denitrogenation of real fuels via liquid–liquid extraction, using acidic DES [51]. The utilization of a mixture of tetrapropylammonium bromide and acetic acid allowed them to achieve complete removal of pyrrole and pyridine in only two extraction stages, as well as achieving 89% removal of thiophene after five cycles of 1 h each at 298 K, showing an increase in desulfurization compared to the previous work from Warrag et al.

2.3. Other Solvents

Following the search for nonionic solvents able to perform simultaneous extractive desulfurization and denitrogenation, Zhu et al. [52] recently published a study about the application of polyether amine-based solvent. This was considered a green, low-cost, and efficient extraction solvent. The removal of S-containing compounds (72.16% for thiophene, 63.96% for dibenzothiophene, and 53.01% for benzothiophene) and N-containing compounds (98.31% for indole (IND), 97.12% for pyrrole, 91.51% for pyridine, and 89.93% for QUI) was achieved. After five cycles of extraction, the extractive capacity of this solvent was still maintained.

3. Adsorptive Process

Adsorptive denitrogenation (ADN) and desulfurization (ADS) are energetically sustainable methodologies for producing cleaner fuels. Effective materials able to conciliate ADS and ADS require an elaborative chemical structural designer to achieve physicochemical adsorption of organic S- and N-compounds. Most of the solid adsorbents present extensive surface areas, with suitable pore volumes containing appropriate active sites, and must contain structural robustness and stability. Further, these materials must be easily regenerated, allowing their use for consecutive ADN and ADS cycles under conditions of mild temperature and pressure [53]. The adsorptive process presents the advantage of absence of chemical reactions, ensuring the absence of impurities from by-products in fuels and safeguarding the physicochemical properties of treat fuels.

The adsorption of organosulfurs/organonitrogens can be explained through physical and/or chemical processes, namely Van der Waals (V. d. W.) interactions, Lewis acid–base interactions, and π complexation [54]. N-compounds can also be adsorbed through

hydrogen bond formation with adequate surface functional groups [55]. The simplest of these interactions is Van der Waals, a simple physical adsorption process producing weak adsorbent–adsorbate interactions, especially in low-temperature applications [56]. Acid–base interactions are the most common chemical mechanism for S and N adsorption. This adsorption theory postulates that the coordinatively unsaturated metal acidic sites or functional groups in the adsorbent bind with the basic S or N moieties in the adsorbate through Lewis acid–base interactions [55]. π complexation comprises the transfer of electrons between π orbitals N/S-compounds and vacant metal sites in the adsorbent [57]. Understanding these adsorption mechanisms helps direct research towards the rational design of novel adsorbents featuring remarkable textural properties, adequate surface-active sites and defect density, robustness, and stability [58]. Recent research in the field of adsorbents for simultaneous ADS and ADN has focused on carbon-based materials, zeolites, mesoporous silica, and metal–organic frameworks (MOFs), as well as their respective structural tuning towards higher organosulfur and organonitrogen removal capacities.

3.1. Carbon-Based Materials

Carbon-based materials are currently the subject of outstanding interest in the development of novel materials due to their varying properties, associated with morphology and the high variety of functional groups than can be introduced [59]. Both micro- and nanoscale carbon allotropes demonstrate potential towards sustainable sulfur and nitrogen adsorption from liquid fuels [60,61]; thus, examples based on the use of activated carbons, graphene, and carbon nanotubes will now be discussed.

Activated carbons (ACs) have been widely used as adsorbents in liquid-phase adsorptions due to their high surface areas (typically 500–4000 m^2/g) [62]. Large pore volumes can also be found [63]. Beyond their textural properties, the adsorption capabilities of ACs are heavily influenced by the presence of oxygen-containing functional groups. In 1999, Pradhan et al. oxidized ACs using HNO_3, H_2O_2, and $(NH_4)_2S_2O_8$ at different temperatures. The authors noted that, despite a reduction in surface area for oxidized ACs, their oxygen contents could be enhanced nearly three times, increasing their adsorption capabilities. The positive effect of increasing surface oxygen functional groups compensates the negative effect of the decrease in microporosity under mild oxidation [64]. This work served as a basis for Ania et al. to oxidize an AC with $(NH_4)_2S_2O_8$, finding an increase of 74% in DBT adsorption compared to that of the original AC [65]. Li et al. also reported that the adsorption capacities of the basic N-compounds of an AC were effectively enhanced after a similar oxidation procedure [66]. However, Han et al. were the first authors to apply these ACs in simultaneous ADN/S, noting that treating the AC with 15 wt.% $(NH_4)_2S_2O_8$ increased N adsorption by 18% (from 0.40 $mmol \cdot g^{-1}$ to 0.47 $mmol \cdot g^{-1}$) but reduced S adsorption (from 0.18 $mmol \cdot g^{-1}$ to 0.16 $mmol \cdot g^{-1}$) capabilities [67]. The adsorption of simultaneous N- and S-compounds present in the liquid matrix follows distinct principles; while N adsorption is mostly dominated by the presence of oxygen from functional groups presented on the surface of ACs, the adsorption of S-compounds depends mostly on the textural aspects [67]. This suggests that ACs can be tailored to maximize adsorption of both classes of compounds simultaneously. Metal loading on ACs is another interesting route which aims to enhance their adsorption strength and selectivity and/or to introduce reactive adsorption routes via the incorporation of metallic species into the carbon matrix. Thaligari et al. prepared a Zn-impregnated granular AC and tested it as adsorptive material for DBT and QUI, demonstrating the competitive nature between the two species and noting that N-compounds are more favorably adsorbed than S-compounds [68]. A similar outcome was observed by Arcibar-Orozco when iron nanoparticles were introduced into an AC. In this case, a higher desulfurization and denitrogenation efficiency was observed when the processes were conducted separately. Performing simultaneous ADN/S, a reduction in sulfur adsorption was found using the modified AC. Furthermore, increasing the total nitrogen content present in the model fuel, the desulfurization capacity of the ACs decreased [69].

Nanoscale carbon allotropes have also been extensively explored for adsorption studies since these possess similar surface functionalities to ACs. Graphene is the building block for the graphitic materials of every other dimensionality, producing adsorbents with unique mechanical properties and extensive surface areas (theoretically as high as 2630 m^2/g) [70], chemical inertness, and remarkable electrical and thermal conductivities [71]. Chemical treatment of graphite through oxidation, with subsequent dispersion and exfoliation in water or suitable organic solvents, produces graphene oxide (GO), a functionalized form of graphene, which is decorated with oxygen-containing functional groups [72]. Nanoscale carbons have been extensively studied as adsorptive materials for single ADS [73]; however, their application towards ADN seems to significantly lag behind. Li et al. prepared hollow mesoporous carbon nanospheres (HMCNs) that were further oxidized with HNO_3, H_2SO_4, and $(NH_4)_2S_2O_8$ to introduce oxygen-containing groups and obtain stronger acidity, promoting acid–base interaction and hydrogen bonding between the adsorbents and QUI/IND molecules. Interestingly, the presence of sulfur compounds in the matrix did not significantly affect nitrogen compound adsorption performance, unlike what was previously observed for ACs. However, HMCNs also preferentially adsorb nitrogen over sulfur compounds (Figure 4) [74].
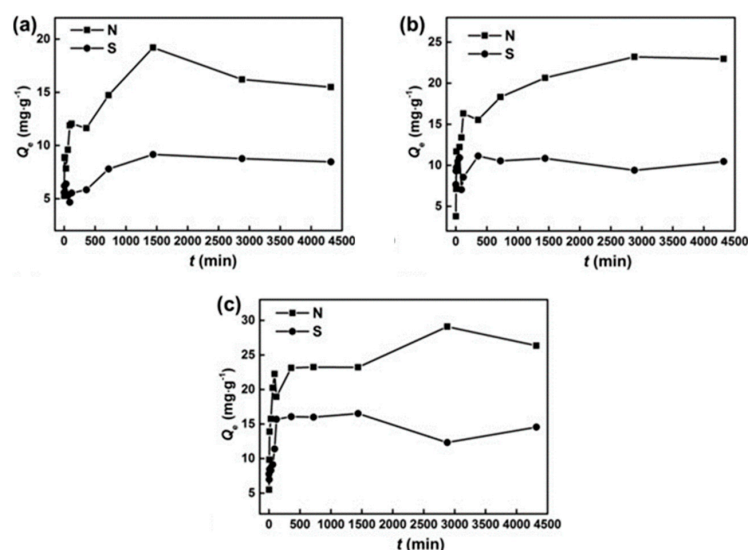
Figure 4. Adsorption curves of NCCs and SCCs over oxidized HMCNs at (**a**) 50 °C, (**b**) 100 °C, and (**c**) 150 °C. Reproduced from reference [48].

To the best of our knowledge, the only work reporting simultaneous ADN/S with nanoscale carbon materials involved the formation of a graphene oxide (GO) composite and the MOF MIL-101 [75]. The composite displayed increased NCC adsorption capacities (~42% higher than the pristine MOF) due to the combined effect of the increase in porosity and the inclusion of hydrogen bonding capabilities from the added oxygen containing surface functional groups. When this adsorbent was applied in a model oil containing QUI, IND, and 1-BT, it was found that the presence of the SCC did not affect NCC adsorption. However, the adsorption of 1-BT was negligible [75], in accordance with previously mentioned studies for the simultaneous adsorption of NCCs and SCCs using carbon-based materials. In conclusion, studies using carbon materials, in general, will need further research towards the development of novel modification strategies in order to produce adsorbents with higher capacities to simultaneously remove NCC and SCC ADN/S.

3.2. Zeolites

Zeolites are microporous three-dimensional crystalline aluminosilicates with high external surface areas (150–500 m^2/g) which are commonly used as adsorbents and catalysts. These types of materials are some of the most investigated for ADS due to their stable

skeleton structure and different shapes (channels, cages, cavities, etc.) and sizes. Zeolites present remarkable thermal, mechanical, and thermal properties, as well as the ability to perform ion exchange on surface active sites, which significantly boosts their adsorption capacity and selectivity towards S- or N-compounds [76].

Synthetic zeolites are widely employed as adsorbents in a variety of adsorption processes, as careful control of the conditions of their processing allows for control of the structure and surface characteristics of the obtained adsorbent [77]. Plenty of research has been conducted on the use of zeolites for ADS processes, and a recent review by Dehghan et al. has effectively condensed the important parameters which influence the sulfur adsorption capacity for a given zeolite: texture properties, pore size, Si/Al ratio, the number of active surface sites, their acidic properties, and the charge of introduced metal cations [78]. The influence of each of these parameters has been confirmed through computational methods by Mguni et al., who developed a machine learning method to reach a consensus on the parameters with dominating influence on the S adsorption capabilities of a given zeolite. Beyond the previously mentioned parameters, this machine learning algorithm also identified the initial adsorbent concentration as the main parameter of adsorption efficiency [79]. As in the case of carbon-based materials, ADN research using zeolites significantly lags its ADS counterpart. Hernández-Maldonado et al. prepared a Y zeolite containing cuprous cations through ion-exchange procedures and tested its adsorption capacity for pyrrole, aniline, carbazole, and IND, comparing it with thiophene. The researchers found that, similarly to metal-doped carbon-based materials, CuY zeolite preferentially adsorbs organonitrogens. They suggest that, since adsorption follows the classical picture of π complexation, zeolites with other d-block cations are expected to preferentially adsorb the organonitrogen compounds as well, which is in accordance with the molecular orbital theory [80]. Zhang et al. had previously reported that a Cu-exchanged Y zeolite could adsorb ~50% more DBT than the pristine adsorbent, and the adsorption of SCCs using d-block metal exchanged Y zeolites mainly occurs through π complexation [81], which could explain the simultaneous deep ADN/S. Zhang et al. studied the effect of ion-exchanged Y zeolite with cerium [82] on ADN, since it was previously reported that the incorporation of La^{3+} species into aluminosilicate positively affected its sulfur adsorption capacity due to the introduction of the possibility for direct interactions between the lanthanum ions and the adsorbents [83,84]. The researchers found that increasing the amount of Ce in the adsorbent did not necessarily imply an increase in denitrogenation efficiency (Figure 5). Increasing Ce loading above the optimum value (7.46 wt.%), agglomeration of CeO2 particles occurred on the surface of the adsorbent, resulting in a decrease in adsorption properties. CeY zeolite achieved ADN efficiencies near two and two and a half times higher than its pristine counterpart for the adsorption of QUI and IND, respectively.
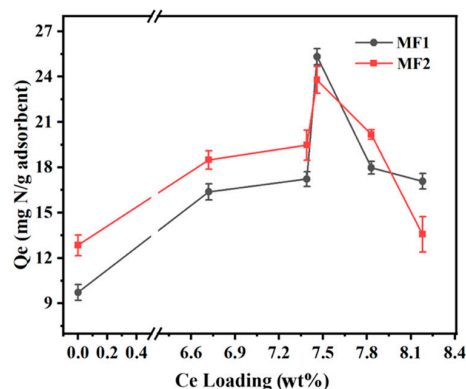
Figure 5. Effect of Ce loading on the N adsorption capability of Y zeolite for two different model fuels (200 ppm of QUI or IND for MF1 or MF2, respectively). Reproduced from reference [82].

The QUI adsorption capacity of the spent CeY zeolite in its third cycle (14.01 $mg_N\,g_A^{-1}$) was still higher than that of the original NaY adsorbent (9.72 $mg_N\,g_A^{-1}$). This ion-exchanged zeolite was especially selective towards NCCs in the presence of naphthalene, a competitive aromatic component. The selectivity towards the adsorption of NCCs over other aromatic compounds was also demonstrated by Tian et al., who incorporated Yttrium into Y zeolite. This incorporation led to a decrease in BET surface area and pore volume, compensated for by the introduction of strong Brönsted acidity and medium Lewis acidity. When used as an adsorbent in a model fuel containing NCCs and toluene, its capacity to adsorb NCCs was maintained, unlike in the pristine zeolite, which lost near 10% adsorption capacity for QUI and near 30% for IND, demonstrating the importance of acid–base interactions in the adsorption selectivity of zeolites [85]. The literature review for simultaneous ADN/S with zeolites leads to similar observations to those of carbon-based materials: their selectivity towards NCCs significantly harms their simultaneous adsorption capabilities.

3.3. Mesoporous Silica

The large specific surface area (700–1300 m^2/g) and pore volume (0.5–1.2 cm^3/g), tunable pore size, and narrow pore distribution of mesoporous silica materials have granted a vested research interest in these materials for ADN/S [86]. Kwon et al. first tested the simultaneous adsorption capabilities of a spherical mesoporous silica (YSP-1) over treated (hydrodesulfurized fuel < 10 ppm N and <1900 ppm S) and untreated (190 ppm N and 8200 ppm S) fuels [87]. This silica-based adsorbent, with a surface area of 1331 $m^2 \cdot g^{-1}$ and an average pore size of 24 Å, adsorbed 8.14 $mg_N\,g_A^{-1}$ from the untreated fuel, much higher than that for a previously reported silica–zirconia co-gel (3.71 $mg_N\,g_A^{-1}$, S_{BET} = 502 $m^2\,g^{-1}$) [88]. This result demonstrates the importance of extensive surface areas for effective adsorption. Zirconia cations were introduced into the mesoporous structure of YSP-1, producing YSP-2 (average pore size and surface area of 31 Å and 1092 $m^2\,g^{-1}$, respectively). YSP-2 adsorbs 29% more of S (7.74 $mg_S\,g_A^{-1}$) than YSP-1 (5.99 $mg_S\,g_A^{-1}$) while retaining similar N adsorption capacity, suggesting that metal incorporation in silicas is a viable strategy for producing simultaneous ADN/S adsorbents. Koriakin et al. took a similar approach, incorporating lithium into YSP silica and introducing adsorbate–metal interaction capabilities [89]. Compared to the original YSP, the YSP-Li possessed a smaller surface area (815.16 m^2/g) and a larger pore size (3.73 nm). The adsorption capacity of this silica was compared to that of lithium impregnated in siliceous foam (Li-MCF) (551.59 m^2/g and 19.62 nm surface area and pore size, respectively). YSP-Li adsorbed near 41% of NCCs, higher than what was observed for MCF-Li (25.9%). The removal percent for sulfur compounds was negligible for both adsorbents. The literature review on silica-based adsorbents for simultaneous ADN/S is in accordance with previously discussed examples: NCCs are more favorably adsorbed than SCCs, even on functionalized materials.

3.4. Metal–Organic Frameworks

MOFs are a class of porous 3D materials produced from the combination of multidentate organic linkers and metal ions/clusters. The huge number of possible linker/metal combinations ensures that multiple topologies can be produced, which are often accompanied by thermal, chemical, and mechanical resistance, extensive surface areas, and tailorable porosity [90]. These novel materials have garnered considerable interest in several areas of applications, with adsorption among them. In fact, the potential of MOFs for ADS has already been covered in a recent review by Saha et al. [18] Thus, this review will now focus on their application in ADN and simultaneous ADN/S. One of the first and most thorough investigations into the potential of MOFs for simultaneous ADN/S was reported by Maes et al. in 2011. The researchers compared the adsorptive capacity of various MOFs: MIL-100 with different metal centers (Fe, Cr, Al), MIL-101(Cr), MIL-53, HKUST-1, and CPO-27 with either Ni or Co. They found that MOFs with open metal sites (i.e., all studied MOFs except MIL-53) display a significantly higher uptake of both NCCs and SCCs than those without open metal sites (i.e., MIL-53). Furthermore, the selectivity of MOFs containing

Al^{3+}, Cr^{3+}, and Fe^{3+} for NCCs was demonstrated and explained through Pearson's concept of hard/soft acid/bases (hard N bases prefer interactions with hard Lewis's acid sites). In fact, the selectivity and remarkable adsorption capacity of MIL-101 for NCCs from fuels had already been reported by Nuzhdin et al., producing an adsorbent with one of the highest N uptakes to the date of publishing [91]. Following a comparative research line, Jhung et al., attempted to understand the effect of the acidity or basicity of MOFs on their ADN capabilities. MIL-100(Cr) was modified to impart acidity or basicity by grafting ethylenediamine (ED) and aminomethane sulfonic acid (AMSA) onto its coordinatively unsaturated sites. Despite a decrease in BET surface area (from 1462 m^2/g to 1351 m^2/g), the acid-functionalized MOF (AMSA-MIL-100) displayed an effective increase in the adsorptive removal of QUI (from 160 mg·g$_A$$^{-1}$ to 190 mg·g$_A$$^{-1}$) and BT (from 18 mg·g$_A$$^{-1}$ to 23 mg·g$_A$$^{-1}$) due to the introduction of acid–base interaction functionality. The introduction of basic functionalities (ED-MIL-100) decreased the adsorption performance of the MOF due to base–base repulsion with the basic adsorbates. Interestingly, functionalization of the MOF with either acid or basic groups decreased its IND adsorption capabilities, as this neutral NCC was preferentially adsorbed by Van der Waals interactions; thus, higher surface areas were the determining factor for its adsorption [92]. Ahmed et al. imbued MIL-125 with H-bonding capabilities by modifying its linker with −NH$_2$ functional groups. The researchers verified that the adsorbed quantities of both IND and QUI increased in line with increasing the content of the −NH$_2$ group in the MOF [93]. Mondol et al. took this approach a step further by introducing amino groups on both the ligand and metal sites of MIL-101(Cr). This functionalization caused a decrease in BET surface area (from 2488 m^2/g to 1960 m^2/g) but significantly increased IND adsorption while decreasing QUI removal, similar to the previously discussed research study. The MOF was further modified by the introduction of carboxylic groups (Figure 6), which boosted its NCC adsorption capacity to nearly double that of the pristine structure and about 10 times as much as that of a commercial AC, due to the introduction of H-bonding functionality in the adsorbent [94].
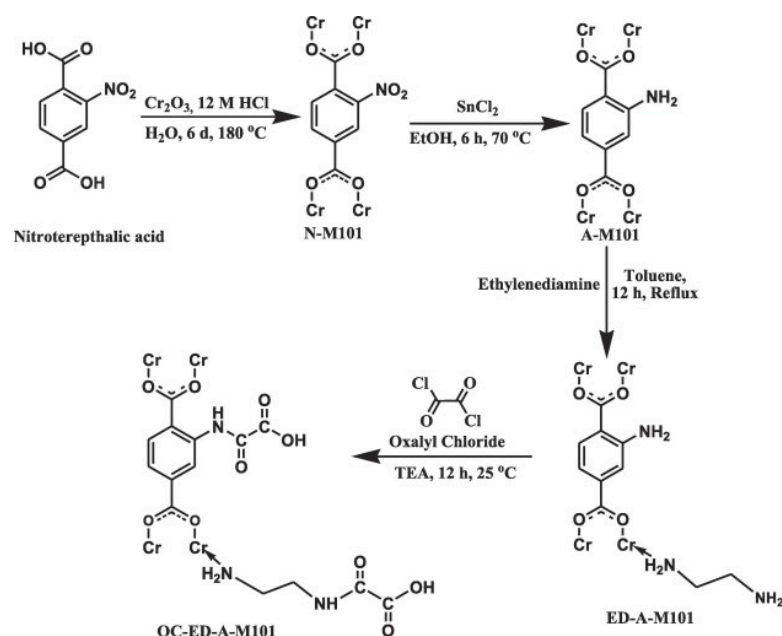
Figure 6. Representation of reaction route to prepare a difunctionalized MIL-101 derivative. Reproduced from reference [94].

We have thus far discussed research work that demonstrates IND adsorption is favored over adsorbents containing −NH$_2$, −COOH, −OH, and −SO$_3$H groups in MOFs of the MIL family. This behavior is not exclusive to this family, as different MOFs have been subjected to similar design strategies to ensure their optimal ADN/S performance.

Sarker et al. modified UiO-66 with several functional groups ($-NH_2$, $-NH_3^+$, $-COOH$, $-COONa$, $-OH$, $-SO_3H$) to quantitatively understand the interactions between the adsorbates (IND and QUI) and UiO-66. Despite having lower BET surface areas and micropore volumes than the pristine MOF, the modified structures displayed generally better adsorption performance. UiO-66-NH^{3+} showed exceptional adsorption of IND due to cation$-\pi$ interactions [95]. This type of cationic$-\pi$ interaction has also been applied to interpret the high IND adsorption over protonated MIL-125 [93].

The literature review suggests MOFs might be one of the most promising candidates with regards to achieving the application of adsorption-based methodologies in the removal of NCCs and SCCs at an industrial level; however, from a general standpoint, it must be stated that the selectivity of all discussed materials for organonitrogens severely limits the interest in simultaneous ADN/S. Applying ADN at an industrial level could be an interesting approach to selectively removing NCCs before HDS, protecting refinery equipment and catalysts. However, if the simultaneous removal of both types of species is the goal, the synergistic combination of processes based in adsorption with extraction and/or oxidation appears to be a more auspicious research path.

A comparison of the reported ADN and ADS results previously discussed in this section is illustrated in Table S1 (displayed in Supplementary Information document, SI).

4. Catalytic Oxidation Process

Oxidative desulfurization (ODS) is among the studied techniques dedicated to the elimination of S-compounds from fuels. It might be one of the most promising methods for desulfurization when combined with liquid–liquid extraction, presenting advantages like mild and simple processing as well as high efficiency in removing refractory sulfur compounds, including Th, BT, DBT, and 4,6-DMDBT [29,96–105]. However, an efficient and sustainable process capable of simultaneously executing oxidative desulfurization and denitrogenation (ODN) of fuels is in fact an actual necessity in the refinery industry. ODN was studied more scarcely than ODS; there were only a few studies dedicated to the ODN and both techniques simultaneous [26,106–117], probably due to the different chemical natures of oxidized sulfur compounds (OSCs) and oxidized nitrogen compounds (ONCs). The S-compounds can be oxidized into sulfone or sulfoxide in fuel, whereas N-compounds can seldom be oxidized into nitrogen oxides (see Figure 7). Moreover, during ODN, catalysts might be deactivated, especially by very reactive N-compounds that can react very strongly with common metal-based catalysts, thereby making it difficult to find suitable catalysts or methods for ODN. The oxidized products are then removed via adsorption or extraction from model oil. The oxidation reaction occurs in mild operating conditions (less than 100 °C and at atmospheric pressure) and in the presence of oxidants such as H_2O_2, tert-butyl hydroperoxide (TBHP), and in some instances, molecular O_2 or O_3. This session describes the reported results of simultaneous removal of S- and N-compounds from model diesel under the oxidation method.
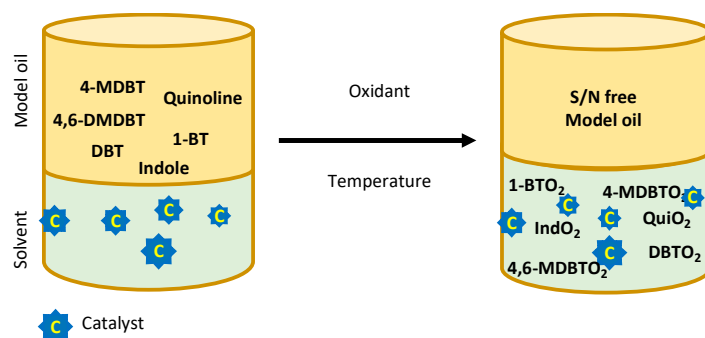
Figure 7. Scheme of simultaneous ODS and ODN processes of a biphasic system of a model oil containing S- and N-compounds.

In 1973, Guth and Diaz [118] patented the oxidation process with a gaseous mixture of oxides of nitrogen to oxidize sulfur and nitrogen in fuel oils, which were then removed with methanol. Years later, carbon-based materials have proved to be interesting materials that can be used in ODS and ODN processes under different systems. Guimarães et al. prepared a series of magnetite covered with carbon as a catalyst for the simultaneous oxidation of DBT (50 ppm) and QUI (50 ppm) in a biphasic system (water/toluene) with H_2O_2 and acetic acid as oxidants [119]. The conversion of DBT was higher than QUI conversion (100 and ~60%, respectively). The authors justified the results with the amphiphilicity of the catalyst and its ability to remain in the interface between the two solvents, one of the critical conditions for displaying high catalytic activity.

In 2017, Raffie and Khodayari investigated the influence of N-compounds (IND, QUI, pyridine, and pyrrole, 60 ppm) on the removal of DBT (1000 ppm) from a simulated model diesel using $PMoV/Fe_3O_4/g\text{-}C_3N_4$ as catalysts [120]. All nitrogenated compounds were oxidized in only 20 min. The reaction rate for the oxidation of DBT in the presence of these N-compounds decreased in the following order: IND > QUI > pyrrole > pyridine. These results suggest that N-compounds have a negative effect on the ODS process owing to competition with the sulfides for adsorption on the catalytic sites, as well as their basic character. The presence of N-compounds reduced DBT oxidation, but the effect was minimal [120]. This group reported a previous study using an $HPW/TiO_2/GC$ catalyst in similar conditions [121]. They have also concluded that the addition of nitrogenated compounds slightly impacts DBT removal. However, they have not reported the conversion of those nitrogenated compounds in the system. Cho et al. (2014) conducted a similar study with a Ti-SBA-15 catalyst and TBHP as the oxidant to remove S- and N-compounds from model fuel [122]. They also reported that ODS activity was drastically decreased due to the competitive oxidation and the deposit of the oxidized S- or N-compounds on the catalyst surface, poisoning the adsorption sites where reactive oxygen species are formed.

There are some studies using oxides as catalysts in the simultaneous ODS/ODN processes from model diesels. Cedeño Caero et al. (2006) reported that N-compounds have a negative effect on the oxidation of S-compounds from model diesels [123]. They studied the effect of the oxidant reagent (H_2O_2 and TBHP) and the presence of N-compounds on ODS of a model diesel (prepared with 936 ppm S) carried out under mild conditions (atmospheric pressure and 60 °C). This reaction occurred in the presence of V_2O_5/Al_2O_3 with V_2O_5/TiO_2 catalysts and acetonitrile as the solvent. After 1 h, the ODN activity decreased in the following order: QUI > IND > carbazole. This effect was explained by the successive chemisorption of DBT and quinoline on the surface of the V_2O_5/Al_2O_3 catalyst, and the results show that DBT was displaced by quinoline, occupying the adsorption sites of the catalyst. Thus, the presence of N-compounds did not influence the ODS reaction mechanism, since only IND was oxidized, and all N-compounds inhibited the ODS reaction. The N-compound effect could be explained by the strong adsorption of N-compounds on catalytic sites but also by their basic character. The authors attributed the lower activity to the poisoning of the active sites by N-compounds. Jia et al. also encountered similar catalytic behavior when removing the typical S-compounds in the presence of nitrides [124]. That study used Ti-containing molecular sieves (Ti-HMS) as the catalyst and H_2O_2 as the oxidant. The effects of nitrides on ODS also suggested a preferentially strong adsorption of N-compounds and their oxidized products on the active sites of the catalysts. Palomeque-Santiago et al. removed S- and N-compounds present in diesel fuel and straight-run gas oil (SRGO) using WO_x/ZrO_2 catalysts and H_2O_2 via ODS and ODN reactions [125]. Diesel fuel and SRGO were desulfurized and denitrogenated with high efficiency: 97% in diesel fuel and 70% in SRGO for S-compounds and 96% in diesel fuel and 89% in SRGO for N-compounds, whereas C_1–C_3 DBT, 4-MDBT, and 4,6-DMDBT were fully removed [125]. On the other hand, Ishihara et al. reported that N-compounds could be oxidized in the ODS system [109]. They developed a flow-type process in which the oxidation reactor was combined with an adsorption reactor disposed in-line, as well as a continuous oxidation/adsorption process. This method oxidized the refractory DBT

compounds remaining in a pre-desulfurized light gas oil (LGO) with TBHP as the oxidant in the presence of 16 wt.% MoO_3/Al_2O_3 catalyst at 80 °C. The same experimental procedure was also successfully used to remove N-compounds from model diesel, as well as in the LGO, with great efficiency. The total sulfur content could be decreased to values less than 5 ppm (initial S content $\sim$39 ppm). The ODN activity of the N-compounds decreased in the order of IND >QUI >acridine >carbazole, showing that the carbazole was the most difficult to oxidize. Moreover, after the complete process, the nitrogen concentration in the LGO could be decreased from 13.5 ppm to a value as low as 0.8 ppm. However, the oxidation products of N-compounds were not fully identified, suggesting the presence of polymeric compounds. Subhan et al. reported the selection of an ideal catalyst/oxidant system for the energy-efficient ODS of DBT and ODN of pyridine [126]. They used Mn-Co-Mn/Al_2O_3 and acid-functionalized ([BMIM]Cl/$ZnCl_2$) ionic liquid as catalysts and H_2O_2 and NaClO as oxidants. Catalytic activity and dynamic studies revealed good synergism between the NaClO–catalyst systems, which achieved 100% DBT and pyridine conversion in 15 min at 25 °C, as compared to H_2O_2, where [BMIM]Cl/$ZnCl_2$ exhibited greater affinity for N-compounds due to the nucleophilic behavior of cationic species. Dynamic studies revealed lower activation energy values for the removal of DBT and pyridine in the presence of NaClO over Mn–Co–Mo/Al_2O_3 and [BMIM]Cl/$ZnCl_2$ as catalysts. Based on the excellent ODS and ODN activity results, cost-effectiveness in terms of low energy consumption, simplified mechanization, and greenness, the proposed study can be envisaged to be of great help for fuel oil processing on the industrial level. More recently, Safa et al. (2021) also used the MoO_3/Al_2O_3 catalyst to study the effects of co-existing N-compounds and PAHs on ODS of 4-MDBT and 4,6-DMDBT in the middle distillates (with cumene hydroperoxide as oxidant) [127]. The results indicate that there is a competitive adsorption of N-compounds and PAHs (Polycyclic aromatic hydrocarbon) with the S-compounds, and both compounds have a stronger inhibition with the oxidation of 4-MDBT than 4,6-DMDBT. The authors found that N-compounds were involved in the ODS process and that it could be simultaneously removed from the system.

Shiraishi et al. also successfully investigated ODS and the simultaneous ODN process for three different light oils based on the chemical oxidation of S- and N-compounds using H_2O_2 and acetic acid, followed by extraction of the resulting compounds. The ODN yields were higher than the ODS yields for all the light oils [128]. Nitrogen content of light oils was reduced to <22%, and sulfur content failed to be reduced to the required deep desulfurization level (0.05 wt. %). This happened because the sulfones produced during the oxidation of S-compounds remained in the light oils owing to their high hydrophobicity. When TBHP was employed as the oxidant, the carbazoles, especially those having a large carbon number of alkyl substituents, were the most difficult compounds to remove from fuels.

Rafiee et al. [120], Cedeño Caero et al. [123], and Cho et al. [109] observed low yields for ODS reaction in the presence of various N-compounds. Their results suggest that N-compounds inhibited the ODS, which was attributed not only to competitive adsorption between S- and N-compounds for catalytic sites, but also to their basic character. Therefore, Bertleff et al. studied the influence of IND and QUI derivatives on the extractive oxidative desulfurization reaction [129]. Another process developed by this group combined extractive catalytic ODS and ODN experiments (ECODS/ECODN) in the presence of S-compounds (BT, DBT, and 4,6-DMDBT; 0.25 mmol) and N-compounds (1-methylindole) using $H_8PV_5Mo_7O_{40}$ as a catalyst (HPA-5; 0.5 mmol) [129]. The experiments were carried out with a water/paraffinic diesel fuel ratio of 100 mL/10 mL at 120 °C and 20 bar oxygen partial pressure. The 1-methylindole in the paraffinic diesel fuel promoted the ODS process catalyzed by HPA-5. The catalytic activity after 24 h increased from 78 to 88%. This behavior can be explained by the formation of highly active catalyst species. BT, DBT, and 4,6-DMDBT were removed from the paraffinic diesel fuel faster in the presence of 1-methylindole. Furthermore, 1-methylindole was removed completely from the paraffinic diesel fuel just 5 min after the reaction temperature in the reactor was reached. Moreover,

no decomposition of the paraffinic diesel fuel matrix occurred during simultaneous ECODS and ECODN.

There are some successful studies using different materials as catalysts in this oxidation system, such as oxides supported in carbon, MOFs or silica, and POMs in MOFs, membrane, or oxide. Yaseen et al. synthetized Mn_3O_4 on graphene oxide (GO); this composite was used as a catalyst in ODS and ODN tests [130]. The Mn_3O_4/GO-NaClO system removed 2200 ppm of DBT and pyridine in 2 min at 25 °C. The selectivity for S- and N-compounds followed an order of DBT (100%) > 4,6-DMDBT (89%) > BT (85%) and pyridine (100%) > IND (83%) > carbazole (81%). Recyclability and catalyst stability were recorded for sixth consecutive runs with minimal loss in activity (100–92%), and the catalyst was found to be highly stable. This recent study can be considered a promising process for efficient simultaneous removal of sulfur and nitrogen compounds from fuel oils with a great degree of simplicity, cost-effectiveness, and process safety [130]. One year before, Subhan et al. (2021) studied a similar system [131]. The composite MnO_2/UiO(Zr)-66 was prepared and used as a catalyst in ODS and ODN of fuel oil using NaClO as the oxidant. Catalytic results showed that MnO_2/UiO(Zr)-66 composite oxidized 2000 ppm of DBT (347 ppm S) and pyridine (502.8 ppm N) in 3 min at 25 °C. The mechanism behind the super-fast and highly efficacious performance of MnO_2/UiO(Zr)-66 is the ideal synergy among Mn^{4+}, Zr^{4+}, and NaClO species, which produced strong oxidizing $\bullet OH$ and $\bullet O^{2-}$ radicals. After optimizing the reaction parameters, a much higher removal of DBT and pyridine (100%) was achieved as compared to that of BT, 4,6-DMDBT, IND, and carbazole up to their sixth cycles (the catalyst had a minimal loss in activity after five consecutive reusing cycles and delivered stability and regeneration performance). This study also provided an important oxidative catalytic system, MnO_2/UiO(Zr)-66/NaClO, that showed high catalytic performance and cost-efficiency for use in large-scale ODS and ODN of fuel oils. Rafiee and Rahpeyma prepared a new magnetic catalyst of silica-coated $CoFe_2O_4$ nanoparticles and used it as a support for the immobilization of 12-tungstophosphoric acid (CoFe/Si-PW) [132]. The catalyst showed high activity in ODS of model oils under mild conditions, using H_2O_2 as an oxidant. The effect of N-compounds on ODS via adding QUI and IND to the oxidation system was studied. The results suggest that QUI inhibited ODS more than IND did. This was attributed to competitive adsorption between S- and N-compounds for catalytic sites. For the first time, the research group of Balula et al. incorporated an ionic liquid polyoxometalate (IL-POM) in the ZIF-8 and applied it as the catalyst for simultaneous ODS and ODN processes [117]. The heterogeneous catalyst [BMIM]PMo_{12}/ZIF-8 revealed exceptional catalytic efficiency to concurrently proceed with the ODS and ODN of a multicomponent model diesel containing various S- and N-compounds. All these compounds were removed after only 1 h, and the catalyst system was able to be reused for ten consecutive cycles without loss of efficiency. This group also applied an ionic lamellar coordination polymer to remove S and N pollutant compounds from model diesel with high efficiency [116]. Its oxidative catalytic performance was investigated using single sulfur (1-BT, DBT, 4-MDBT, and 4,6-DMDBT, 2350 ppm of S) and nitrogen (IND and QUI, 400 ppm of N) model fuels, as well as multicomponent S/N model diesel. Complete denitrogenation was achieved after 2 h (99% after 1 h), and at the same time, the desulfurization attained 88% (92% after 3 h) using model fuel with S- and N-compounds, as well an ionic liquid as the extraction solvent ([BMIM]PF_6) and H_2O_2 as the oxidant. Simultaneous processes revealed that the N-compounds were more easily removed from the fuel phase to the ionic liquid [BMIM]PF_6 phase, and consequently, these were oxidized faster than the S-compounds. Identical simultaneous S/N removal was achieved using H_3PMo_{12}@MOF-808 [133] and H_3PMo_{12}@MIL-100 (Fe) [134], achieving complete removal of S and N from multicomponent fuels after a few minutes. The high efficiency of these catalysts was conciliated with an effective extraction ionic liquid [BMIM]PF_6 solvent that received oxidized and non-oxidized S- and N-compounds. Between both heterogeneous catalytic systems, the H_3PMo_{12}@MIL-100 (Fe) was shown to allow a higher number of recycling cycles without the loss of efficiency [133,134].

The reusability of the fuel/H_2O_2/[BMIM]PF_6 system catalyzed using lamellar catalysts was more efficient for ODN than for ODS processes using a multicomponent model fuel. The reuse capacity of this system was catalyzed by lamellar material loss efficiency in consecutive ECODS cycles, probably caused by the saturation of the extraction [BMIM]PF_6 phase with S- and N-compounds. Aghbolagh et al. successfully designed and synthesized a new green catalyst, TBAPMo$_{12}$Cu/CuO, to be used in simultaneous ODS and ODN of model oils (DBT, thiophene, pyridine, and carbazole) in the presence of PEG-200 as an extraction solvent and H_2O_2 as an oxidant [135]. This new catalyst demonstrated an excellent catalytic activity and long-term stability for producing ultraclean fuels obtained with the following conversion: thiophene (97%) > DBT and carbozole (98%) > pyridine (99%) within 1 h at 35 °C. Excellent performance of the catalyst for oxidation processes was verified based on the agreement between experimental data and computational results. Based on the results, the removal of a considerable amount of S- and N-compounds was possible via catalytic oxidation–extraction; however, simple solvent extraction (using methanol, ethanol, and acetonitrile) was inadequate for deep denitrogenation. The TBAPMo$_{11}$Cu/CuO catalyst showed excellent reusability for five oxidation cycles. Banisharif et al. studied the ECODS of model oil with S- and N-compounds (BT, DBT, 4,6-DMDBT, and QUI) using PWV$_5$@TMA-Si as the catalyst and H_2O_2 as the oxidant under atmospheric pressure and temperatures lower than 100 °C [136]. In the absence of the solvent, the oxidation was 100% for QUI and 80% for the S-compounds, using a model oil containing 500 ppm of S. Increasing the S content to 1500 ppm, only 70% of the total S was removed after 30 min of reaction. However, when acetonitrile was employed as an extractive solvent, the ODS was increased considerably, removing approximately 100% of QUI and 95% of S from 500 ppm model oil (87% of sulfur using model oil with 1500 ppm of S) after 30 min. The catalyst PWV$_5$@TMA-Si was shown to be very active for ECODS and could be reused five times without apparent decrease in activity when using 500 ppm of S model oil. Yao et al. demonstrated for the first time the highly efficient application of POMs supported by layered double hydroxide (LDH) composites (LaW$_{10}$@LDHs) in simultaneous ODS (1000 ppm) and ODN (100 ppm) of a complex model oil with an extraction solvent [BMIM]BF_4 ionic liquid [137]. The system yielded ultra-deep ODS/ODN of fuel oil after 60 min at 65 °C, with a corresponding decrease in the content to less than 10 and 1 ppm, respectively. The high efficiency of the heterogeneous catalyst showed high stability during ten cycles without obvious loss of catalytic activity.

A summary of the catalytic activity on simultaneous ODS/ODN processes in the studies referred to above is displayed in Table S2 in the Supplementary Information document. Therefore, it can be concluded that simultaneous ODS/ODN might be a promising method for removing S- and N-compounds from fuels. New catalysts might be developed and applied using this method, and this can be an attractive and promising research topic in the near future.

Photocatalytic Process

Photocatalytic oxidative desulfurization (PODS) and denitrogenation (PODN) are considered promising methods for achieving fuel purification due to their low cost and simple processes, mild conditions, and high efficiency in removing the refractory SCC and NCC compounds. The products of these oxidations are polar molecules or mineralized products, such as sulfones, sulfoxides, and SO_4^{2-} for PODS and NH_4^+ and NO_3^- for PODN, which can be easily removed from fuels via adsorption or extraction. In the last decade, the research has been focused mainly on PODS, and PODN has been scarcely explored. Simultaneous use of both methods is even less studied. To the best of our knowledge, only six reports have considered PODS and PODN in the same study [138–143]. Some of these works tested the same material separately for each separated process involving S or N [138–141], while only two investigated the activity of the catalyst in both reactions simultaneously [142,143]. These studies are briefly described below, and their results are compared in Table S3 in the Supplementary Information document.

Fard et al., prepared several morphologies of copper(II) oxide (CuO) and tested these materials on the oxidation of IND and BT using mild conditions, H_2O_2 as the oxidant, and UV-C light [138]. CuO rod morphology with a high surface area revealed promising results and was then loaded on a titanium zeolite MWW. This composite, CuOrod/MWW, enhanced the performance of the CuO rod, leading to oxidation efficiencies for IND and BT of 100% and 98%, respectively. It could be recycled at least five times without significant loss of activity.

Zhang et al., developed a low-cost and efficient system for PODN and PODS based on Na-doped g-C_3N_4 nanosheets, obtained via a simple calcination method using a mixture of melamine and different amounts of NaCl [139]. The materials were tested under visible light using molecular O_2 as an oxidant for removal of pyridine (Py) or Th. Material with an optimal amount of Na (designated as Na(0.3)-CN, where x is the mass ratio of NaCl/melamine) oxidized 402.1 µg g^{-1} of Py and 461.6 µg g^{-1} of Th within 6 h. The presence of a moderate amount of Na improved the surface energy and the charge transfer ability of g-C_3N_4 and reduced its recombination rate of electron–hole (e−-h+) pairs. From the results of trapping experiments, the authors proposed a mechanism where the h$^+$ are the major active species for denitrogenation and desulfurization processes and the •O_2^- radicals resultant from the combination of O_2 and e$^-$ are responsible for the promotion effect on the final mineralization process. The material showed good stability and recyclability for at least four cycles for the PODN process.

Li et al., investigated the performance of an MXene material, Ti_3C_2, as a co-catalyst of g-C_3N_4 and prepared several Ti_3C_2/g-C_3N_4 composites with different contents of Ti_3C_2 via direct hybridization [140]. PODN and PODS were performed under visible light, and the optimal conditions were achieved for the composite with 5.0 wt.% of Ti_3C_2 at 0 °C, using atmospheric O_2 as an oxidant, for 3 h, leading to the removal of 245.2 µg g^{-1} of Py and 270.7 µg g^{-1} of Th. The material showed good recyclability for both processes for at least six cycles. The authors combined active species trapping experiments, EPR tests, and DFT calculations to propose the same mechanism as described above.

Fakhri et al., prepared several materials by supporting different loadings of phosphotungstic onto the cerium (Ce)-doped MOF NH_2-UiO-66 and investigated their activity as photocatalysts for the photo-oxidation of DBT and QUI under visible light, using molecular oxygen as oxidant [141]. The best photocatalytic activity was achieved for $30PW_{12}$/Ce-NUiO-66, with a loading of 30% weight of PW_{12}, revealing an efficiency of 99% for PODN and 89% for PODS systems under visible light irradiation for 90 min. In this case, Ce acts as a mediator that enhances the transfer of generated electrons, while the MOF improves the surface area and available adsorption sites and increases the responsiveness to the visible light of PW_{12}. The recyclability and stability of the material were investigated for PODN and PODS, and after four cycles, partial decreases to 91 and 86% efficiency were observed, respectively; however, the photocatalyst remained stable. The authors proposed the traditional Z-scheme mechanism as the main pathway for this system.

Wang et al., described the preparation and application of a highly efficient photocatalyst based on Er, W, and N co-doping modification of TiO_2, labelled as Er/W-N-TiO_2, with 1.6% content of Er and 1.0% of W [142]. The desulfurization and denitrogenation ratios achieved 100% under visible irradiation at 343 K, with 7% of the catalyst for 25 min, using H_2O_2 as an oxidant and CH_3OH as the hydrogen donor. The model fuel used was based on pyridine, Qu, thiphene, BT, and 4,6-DMDBT dissolved in n-decane. The authors also studied the effect of the presence of pyridine and quinoline on the desulfurization reaction and concluded that pyridine decreased the TOF of thiophene, while QUI decreased the TOF of 4,6-DMDBT, mainly due to competitive adsorption on active centers. Er/W-N-TiO_2 also revealed very good stability and reusability for both PODN and PODS processes after 10 cycles. The co-doping improved the hole–electron separation and the light absorption range of TiO_2 due to the increase in oxygen vacancies and Ti^{3+}/W^{4+} surface defects, narrower band gap, and higher photo-generated charge transfer, promoting the photocatalytic activity. The mechanism was also proposed. The same group obtained a similar positive

effect by doping N, Carbon quantum dots (CQDs), and the rare earth elements Ir and Pr in TiO_2 [143]. The best photocatalyst, $Ir/Pr-N-CQDs-TiO_2$, achieved ratios of 99.8% for desulfurization and 95.5% for denitrogenation, under ultraviolet irradiation for 50 min, at 373 K, using H_2O_2 as an oxidant. BT, DBT, 4,6-DMDBT, Qu, IND, and carbazole dissolved in n-decane were used as model fuels. The material also revealed good recyclability and stability after 11 runs.

5. Ultrasound-Assisted Process

The application of ultrasound (US) irradiation promotes, in general, the efficiency of chemical reactions, mainly due to the cavitation. This phenomenon can be described as the formation of vapor bubbles inside a liquid that grow in successive cycles, reaching a critical size and then collapsing violently, creating localized hot spots with high temperature (around 5000 °C) and pressure (around 2000 atm) that enable the production of highly reactive radicals, increasing the rate and efficiency of reactions. Ultrasound-assisted oxidative desulfurization and denitrogenation (UAOD) are attractive from an economic point of view, since they do not require hydrogen and expensive catalysts, and they operate at mild conditions with fast operation and high efficiency. They also allow for higher removal of aromatic sulfur compounds than conventional methods [29]. An excellent review of this topic has recently been published where several parameters of the process, such as temperature, ultrasound power and frequency, pH, and initial concentration of sulfur and nitrogen compounds, as well as the role of the phase transfer agent, solvents of extraction, reaction kinetics, mechanism, and fuel properties, are described [29]. This research is mainly focused on desulfurization; simultaneous desulfurization and denitrogenation are scarcely explored, with only two reports from the group of G. Cravotto [107,144]. In one of them, the authors reported the performance of different solid oxidants: oxone, sodium persulfate, and potassium superoxide for UAOD of two model compounds, DBT and 4,6-DMDBT, as well as of a hydrotreated diesel feedstock. Oxone was revealed to be the most efficient solid oxidant tested, allowing the reduction of S and N to less than 10 and 2 ppm, respectively, in 30 min, using the diesel (S + N)/oxidant molar ratio of 1:30 [107]. In the other work, the application of four different sonochemical flow-reactors for the improvement of ODS/ODN was described, using H_2O_2/CH_3COOH as the oxidant, at flow rates ranging from 60 to 800 mL/min, with both the model compound DBT and a diesel sample. Full DBT oxidation and low values of sulfur (≤ 5 ppmw) and nitrogen (≤ 1 ppmw) [144] were achieved. The main common drawback of these two protocols is the diesel mass loss found on the lab scale, which makes them under-competitive in relation to the classic catalytic hydro-refining process, although they can be applied complementarily to the conventional method.

6. Overview and Perspectives

This review easily demonstrates that the volume of work reported for simultaneous desulfurization and denitrogenation processes is limited compared with what has been reported for studies that performed only desulfurization (near 7000 published papers since the 1980s) or only denitrogenation (around 650 published papers since the 1990s). Simultaneous sulfur and nitrogen removal is much more limited, but even then, a considerable spread of various techniques has been used, such as extraction, adsorption, oxidative catalysis, oxidative photocatalysis, and ultrasound-assisted processes. The processes used most are adsorption first, followed by oxidative catalysis. Simultaneous extractive desulfurization and denitrogenation were mainly performed using ionic liquids or deep eutectic solvents as extractive solvents. Both have shown approximately 50% more extraction than the polar organic solvents. The temperature does not seem to have an important influence on the extractive efficiency; however, the ratio of ionic liquid/oil was shown to considerably affect the extraction of sulfur from fuels, but not the extraction of nitrogen. Using the extractive methodology, the extraction of nitrogen was normally faster than sulfur, and during recycling tests, the loss of efficiency was observed mainly for the extraction of

sulfur. Using model fuels, near-complete S/N removal could be found after a few minutes. Simultaneous S/N extraction process was further performed using real fuels, resulting in high efficiency obtained after only 1 h during at least nine extractive recycling cycles, with the exception of thiophene compounds.

From the several materials used in these adsorptive studies, including carbon-based materials, zeolites, mesoporous silicas, and MOFs, the best results for simultaneous adsorption of S/N from fuels were obtained with carbon-based materials, namely with oxidized hollow mesoporous carbon nanospheres and activated carbon (Table S1 in Supplementary Information). When iron nanoparticles were impregnated in the activated carbon, a large improvement in nitrogen adsorption was observed. MOF materials have been shown to be prominent adsorptive materials for the adsorption of N using S/N fuels. A real fuel was also studied using the adsorption processes, and in this case, a satisfactory result could only be observed after 25 h (Table S1 in Supplementary Information). In general, the adsorption processes of S and N needed several hours to occur with satisfactory efficiency. The scale of time to achieve reasonable efficiency was much longer for adsorption than the others already studied, such as extraction, oxidative catalysis, oxidative photocatalysis, or ultrasound-assisted processes. This may be the main obstacle for the industrial application of this process.

On the other hand, using oxidative catalytic processes, high simultaneous desulfurization and denitrogenation efficiencies can be easily achieved after a few minutes (Tables S2 and S3 in Supplementary Information). Recently, the incorporation of catalytically active polyoxometalate into porous MOF support materials has been demonstrated to have the best recyclable catalytic performance for removing the several sulfur and nitrogen compounds present in fuels via simple oxidation. Complete desulfurization and denitrogenation of multicomponent fuels were achieved after 1 h, when the oxidative catalytic process was combined with the liquid–liquid extraction using ionic liquid or ethanol solvents (Table S2 in Supplementary Information). Identical results were achieved using photocatalytic oxidative systems using visible light irradiation (Table S3 in Supplementary Information). Using this process, a more economical catalytic system is normally used; however, the reported examples for simultaneous PODS and PODN required longer reaction times, with the exception using a TiO_2-based catalyst. Complete S/N removal was also achieved after a few minutes under moderate conditions using oxidative ultrasound-assisted processes. However, this technique is practically unexplored for simultaneous S/N removal, and no strong conclusions can be presented based on only the two studies reported in the literature until now. Therefore, a successful future for simultaneously removing sulfur and nitrogen from liquid fuels can be ensured by the combination of an ultrasound-assisted process with photocatalysts, or even active heterogeneous catalysts with high stability and recyclability.

Abbreviations

SCCs, sulfur-containing compounds; NCCs, nitrogen-containing compounds; HDS, hydrodesulfurization; EDS, extractive desulfurization; EDN, extractive denitrogenation; 4,6-DMBT, IL, ionic liquid; DESs, deep eutectic solvents; ADS, adsorptive desulfurization; ADN, adsorptive denitrogenation; 4,6-DMDBT, 4,6-dimethyl dibenzothiophene; BT, benzothiophene; DBT, dibenzothiophene; IND, indole; ODS, oxidative desulfurization; ODN, oxidative denitrogenation; PODS, photocatalytic oxidative desulfurization; PODN, photocatalytic oxidative denitrogenation; UAOD, ultrasound-assisted oxidative desulfurization denitrogenation; QUI, quinoline; Th, thiophene.

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