



Increasing biodegradability of a real amine-contaminated spent caustic problematic stream through WAO and CWAO oxidation using a high specific surface catalyst from petcoke

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ABSTRACT

Different operating conditions of wet air oxidation and catalytic wet air oxidation have been studied for the treatment of highly concentrated methyldiethanolamine wastewater streams from amine units of acid gas recovery in petrol refineries. These units occasionally generate streams of high methyldiethanolamine content that require special actions to avoid undesirable impacts on the downstream biological process of the petrochemical wastewater treatment plant due to its inhibition effect. The wet air oxidation treatment achieved remarkable removals of methyldiethanolamine, sulfides, chemical oxygen demand and total organic carbon (99%, 95%, 65% and 38%, respectively). Likewise, activated petroleum coke materials from the own refinery plant were tested as catalysts in the process. These materials were prepared under different conditions (chemical activating agent and thermal carbonization process). The catalytic wet air oxidation treatment using an activated petroleum coke was able to remove the methyldiethanolamine at milder operation conditions keeping a similar performance in terms of wastewater treatment removals as compared to the non-catalytic experiments. This technology significantly increased the biodegradability of the treated effluents ranging from 25 to 70 % due to the formation of more biodegradable substrates (acetic acid and ammonium) for further biological treatment.

1. Introduction

Despite the foreseen transformation that will take place in the next few years, the reduction in oil consumption will not reach 60 % until 2050, with an 80 % reduction when the energy model is zero emissions to the atmosphere [1]. Therefore, it is necessary to continue processing different highly complex crude oils for years, generating high volumes of complex wastewater that must be treated before discharge [2]. The presence of certain organic and inorganic compounds derived from the production processes can cause inhibition or even toxic effects on conventional biological treatment of centralised refinery wastewater treatment plants (RWWTPs) [3,4].

Among the different residual aqueous streams produced in refineries, the spent caustic streams are considered a hazardous waste due to their complex features [5]. Spent caustic solutions are derived from multiple sources due to the scrubbing of cracked gas in ethylene crackers or

Mercox units processing of liquefied petroleum gas, gasoline, kerosene or natural gas [6]. Spent caustic streams are classified into three types depending on their composition and the process in which they are generated: sulfidic, cresylic, and naphthenic caustic streams. Usually, refineries do not separate each type of spent caustic, and they are mixed for a standard treatment rather than implementing specific solutions for each one [7].

The spent caustic streams contain a high COD, sulfides that produce very strong odors, aromatic compounds such as phenols, amines, calcium carbonate, sulphates and a very high alkaline pH, which makes their handling and treatment extremely difficult due to corrosion and precipitation problems in industrial facilities [8–11]. The amount of sulphates in spent caustic wastewater is not a problem for aerobic biological treatment in RWWTPs [12]. However, in the case of sulfides, there is an internal limit established in some wastewater treatment plants (WWTPs) of 25 ppm to avoid corrosion of concrete and steel,

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safety issues for operators and odours, among other problems [12]. The presence of amines in spent caustic streams is also very important. One of the amines most widely used in crude oil refining processes is methyldiethanolamine (MDEA) [13,14]. MDEA is a tertiary alkanolamine used as absorbent in natural gas sweetening process for removal of hydrogen sulfide (H_2S) and carbon dioxide (CO_2) [14]. Although MDEA is more selective towards H_2S , this amine is also used currently in CO_2 capture processes. This leads to an increase in the arrival of MDEA to WWTPs of the industries in which it is used [15,16]. Regarding toxicity, contradictory reports can be found in the literature. Even though MDEA does not seem to be toxic to aerobic treatment systems [17], certain problems have been identified due to its inhibitory effect on biological processes such as nitrification [18].

Different technologies have been studied for the treatment of spent caustic wastewaters, such as thermally activated persulphate [19], biological treatment based on biomass adaptation to simulated amine concentration [17], ozonation with microelectrolysis [20] and cyclic thermal oxidation processes [21]. In these systems, it must be noted that the highest concentration of MDEA studied was 3,760 ppm from a simulated wastewater working at an acidic pH between 1 and 5 [20]. This concentration is considered in the range of accidentally maximum values found in the inlet streams of biological treatments in RWWTPs.

Wet air oxidation (WAO) has proven to be an effective process for the treatment of wastewater with high organic matter content, allowing the total or partial degradation of compounds that are toxic or refractory to biological processes [22–25]. The elimination of organic compounds identified in the wastewater can be practically total, with COD reductions of more than 70 % in most cases. The removal of MDEA in a real wastewater with higher concentration of the contaminant (in the range of g/L) has been studied in two previous works by a WAO process [26] and a catalytic process (known as catalytic wet air oxidation, CWAO) using a commercial activated carbon as catalyst [27]. In the case of CWAO, most works have been performed using synthetic wastewaters with phenols and derivatives as dominant model pollutants [28]. The operation conditions, type of catalyst and removal efficiencies of all these studies are summarized in Table 1_SM. The catalysts used in this process are normally classified as: noble metal catalysts, non-noble metal catalysts and metal-free carbon materials [29]. Synthesised metal-free carbon materials can promote catalytic wet air oxidation processes for wastewater treatment as an alternative to noble metals and rare earth oxide catalysts. The absence of metals in the catalyst based on carbonaceous materials avoids possible leaching and subsequent treatment needs compared to processes using metal-containing catalysts [28,30].

Petroleum coke (petcoke) is a black-colored solid composed primarily of carbon, generated as a product of the coking process oil refineries or in other heavy hydrocarbon cracking processes at high temperatures and rotational speeds [31]. It contains limited amounts of sulfur, metals, and non-volatile inorganic compounds. The most extensive use of petcoke is as a source of energy or carbon in different industrial applications [32]. Due to the majority use of coke as fuel in industries traditionally considered as a source of pollutant gas emissions, global demand of petcoke is expected to decline and, therefore, finding novel applications is key [33]. To address this danger, potential applications are being studied in which this co-product can be used due to its special characteristics. In this study, the preparation of activated carbon materials in catalytic wet air oxidation (CWAO) for the treatment of wastewater of the own refinery fits into the circularity guidelines that must govern technological processes in the near future. The use of materials prepared from the own refinery petcoke as possible catalysts for the treatment of wastewater has not been already reported despite the large number of studies described in literature (Table 1_SM).

In this work, it is proposed a different approach for the *onsite* treatment of the spent caustic streams containing MDEA in high concentration coming from the natural gas sweetening process, in which accidentally discharges of MDEA could reach concentrations up to 2.6 g/

L. Currently, this highly MDEA-containing stream is mixed with wastewater streams coming from other operation units, diluting the pollutant concentrations upstream of RWWTP. However, mixing is often not sufficient to reduce the concentration to values that can be assumed by a conventional biological process in RWWTPs. The aim of the study is to increase the biodegradability of this wastewater using WAO and CWAO processes. The *onsite* treatment of highly MDEA-containing wastewater streams rather than at the end-of-pipe after dilution would be beneficial from the point of view of reducing the capital expenditures, as lower wastewater flows would require smaller equipment sizes. Additionally, the reuse of a low value-added material such as refinery petcoke as a catalyst in the CWAO process, which is likely to become a waste product owing to increased legislation on emissions, could reduce the operational costs due to the feasibility of using milder operating conditions of pressure and temperature in the oxidation process.

2. Materials and methods

2.1. Materials

Linde Gas España, S.A.U supplied air pressurised bottles for WAO and CWAO experiments. Potassium hydroxide and hydrochloric acid (37 % v/v) used for the petcoke activation, were purchased from Labkem and Sigma Aldrich, respectively.

2.2. Spent caustic wastewater and petroleum coke (petcoke)

The spent caustic wastewater used in this study comes from an amine unit located in a petroleum refinery in Spain. Samples were collected and immediately stored at 4 °C to avoid variations in composition. The so-called fuel grade green petcoke comes from a coker unit of the same petroleum refinery. The petcoke sample was stored in a closed container before use.

2.3. WAO and CWAO of spent caustic wastewater

WAO and CWAO experiments were performed in a 500 mL capacity T316 stainless steel autoclave reactor, resistant to high pressures and temperatures: model 4575A manufactured by the Parr Instrument Company, USA. The reactor was equipped with an electrically heated jacket, a turbine stirrer, and a variable speed magnetic drive. The temperature using a thermocouple immersed in the liquid phase and the stirring rate were controlled using a Parr 4842 controller and the pressure by the gas inlet and a gas release valve located on the top of the reaction vessel. The liquid samples were taken through a dip tube immersed in the reaction mixture. A schematic diagram of the experimental setup is shown in Fig. 1.

Typically, 250 mL of the spent caustic refinery wastewater is placed in the reactor. The pH of the refinery wastewater (9.6 ± 0.1) was not modified and adjusted prior or during the treatment. Initially, nitrogen gas flow was passed through the head space of reaction vessel to ensure inert conditions, and continuous stirring was fixed at 400 rpm. Then, the air was supplied up to 15 bar to maintain the wastewater in a liquid phase. Finally, the reactor was heated to the operating temperature and then the air pressure was increased to the selected value. The temperature and air pressure of WAO and CWAO experiments varied between 150 to 250 °C and 10 to 90 bar, respectively [5]. The same procedure is used for CWAO runs but adding 1 g/L of a carbon-based catalyst prepared from petroleum coke in the initial loading of the wastewater into the reaction vessel. The reproducibility and the accuracy of the performed WAO and CWAO runs were evaluated periodically between tests. Methyldiethanolamine (MDEA), Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), sulfides (S^{2-}) and pH were periodically monitored for samples withdrawn along the reaction time for 60 min. Prior to analyses, the samples were filtered through a 0.7 μm glass fiber filter.

amine content and 36 g/L of TSS. These characteristics allow classify this process stream as a hazardous waste and make it difficult to handle and treat [8,11,36–39].

3.2. Characterization of activated carbon-based catalysts from green fuel petcoke

The fuel-grade green petcoke (PC) collected from a coker unit had the typical characteristics (included in the [supplementary information](#)) of a refinery coke [32], with a low specific surface area (ca. 10 m²/g), a CHNS distribution of 81.7 %, 3.7 %, 1.4 %, and 5.3 %, respectively, and heavy metals content of approximately 1,700 ppm of vanadium and 400 ppm of nickel ([Table 2.SM](#)). Thermogravimetric analyses evidenced, a weight loss lower than 14 % at 1000 °C in an inert nitrogen atmosphere and almost negligible up to 500 °C under air atmosphere ([Fig. 1.SM](#)). [Table 2](#) displays physicochemical characterization of activated carbon materials prepared using different KOH:Petcoke ratios [30]. The chemical activation produced an increase in the specific surface area of the petcoke, due to an increase in the porosity of the material [40]. The increase of KOH:Petcoke ratio from 2 to 4 enhanced the BET specific surface area from 1,043 to 3,459 m²/g. These areas are similar or even higher than those reported for other petroleum cokes chemically activated under different conditions [30,41,42]. Nitrogen adsorption–desorption isotherms ([Fig. 2.SM](#)) depict typical profiles of microporous materials according to the IUPAC. According to the adsorption isotherms, these materials fill the micropores in a continuous process at low relative pressures ($P/P_0 < 0.015$) [43]. According to the Howarth-Kawzoe model, the pore size distribution was centred in the microporous range with values of less than 2 nm ([Fig. 3.SM](#)). The total pore volume of the activated petcoke materials goes from 0.48 cm³/g to 1.63 cm³/g, pore volumes that are up to twice as large compared to other carbonaceous materials obtained by petroleum coke activation [30]. The CHNS elemental analysis showed a significant reduction of N and S contents after chemical activation. Likewise, the content of V and Ni also decreased due to acid washing (HCl) for the removal of KOH. The increase of KOH:PC ratio, calcination temperature, heating ramp and nitrogen flow rate showed a positive effect on the development of more microporous materials with higher total pore volume. A KOH:PC ratio of 4, using a calcination temperature of 790 °C (heating temperature of 20 °C/min and a nitrogen flow rate of 100 mL/min) provide the activated carbon material with maximum specific surface area and total pore volume (3,459 m²/g and 1.63 cm³/g, respectively) and pore size distribution centred at 1.8 nm. X-ray diffraction ([Fig. 4.SM](#)) shows the difference between the structures of the initial petcoke and synthesised carbonaceous materials consisting of graphite microcrystallites characteristic of activated carbon-type materials with a high specific surface area [42]. SEM-EDX analyses of the raw and activated petcoke materials displayed particles of a non-homogeneous morphology and size with a much more porous surface and higher O/C ratios as the KOH:PC

Table 2
Physicochemical characterisation of activated petcoke materials.

Activation conditions				Synthesis results	
KOH:PC ratio (w/w)	Temperature (°C)	N ₂ flow rate (mL/min)	Ramp (°C/min)	Surface BET (m ² /g)	Pore volume (cm ³ /g)
4	790	40	20	2.196 ± 41	1,05
4	790	70	20	2.278 ± 44	1,10
4	790	100	20	3.459 ± 34	1,63
4	700	100	20	3.221 ± 40	1,54
4	610	100	20	1.013 ± 15	0,49
3	790	100	20	1.722 ± 23	0,82
2	790	100	20	1.043 ± 18	0,48
4	790	100	10	1.976 ± 26	1,00
4	790	100	5	1.583 ± 54	0,83

increased by the effect of the activation agent ([Fig. 5.SM](#)).

3.3. Performance of WAO and CWAO on the treatment of spent caustic wastewater

Wet air oxidation (WAO) has proven to be an effective process for the treatment of wastewater with high organic matter content, allowing the total or partial degradation of compounds that are toxic or refractory to biological processes [44]. The WAO process at different reaction temperatures and air pressure was studied for the concentrated MDEA wastewater stream. Additionally, solid catalysts synthesized from green fuel-grade petcoke in the form of microporous activated carbonaceous materials were also tested. [Figs. 2 and 3](#) show the removal of MDEA, COD, TOC, and sulfides of highly MDEA concentrated spent caustic wastewater for WAO and CWAO experiments, respectively. Preliminary blank experiment at 250 °C and 90 bar under inert nitrogen atmosphere showed no modification of the initial characteristics of the wastewater. This indicates a negligible thermal degradation and the need of dissolved oxygen in the wastewater for the oxidation of pollutants.

3.3.1. Influence of the temperature and air pressure on the WAO process

Initially, the highly concentrated MDEA stream was treated at 150 °C under different air pressures ranging from 10 to 90 bar, which can dissolve oxygen amounts from 0.05 to 0.4 mL O₂ per gram of water [45,46]. As it can be seen in [Fig. 2](#), removal of sulfide reached 90 % in all WAO experiments. This fact is attributed to the high reactivity of sulfides as compared to the organic matter contained in the water [8]. This is especially noteworthy for the WAO experiments at the lowest temperature (150 °C), where sulfide removal was above 90 % even with low air operation pressure (10 bar). The increase of air pressure from 10 to 90 bar increased the MDEA elimination but had a slight effect on TOC and COD removals.

Sulfides are dissolved in the wastewater due to the basicity of the waste stream (pH = 9.6). If the pH approaches neutrality (pH = 7), the sulfides can abandon solution as acid gas, which must be treated before emission into the atmosphere [8]. Sulfides may exist in three different forms, H₂S, HS⁻ and S²⁻ depending on the pH of the medium. At a pH of 7, sulfides are present in the form of H₂S gas and HS⁻. If the pH decreases further, most of the sulfides would be in the form of H₂S gas. On the contrary, when the pH increases the majority of the sulfides are in the form of dissolved hydrosulfide (HS⁻) and sulfide (S²⁻) [47]. The treatment of these pollutants has been studied by additions of iron salts for their precipitation [48], biological oxidation [49], neutralization combined with conventional or advanced oxidations such as the Fenton process [47], or by physicochemical separation systems such as electrocoagulation [50]. These processes generate secondary sludge effluents that require a further waste management, increasing treatment costs, consumption of chemicals, etc. Besides, in some cases, the efficiency of sulfide removal is not high enough to make the water amenable for conventional biological treatments. The WAO process overcomes these disadvantages, enabling sulfide removal under mild operating conditions without generating secondary waste effluents [51]. It must be pointed out that for WAO experiments at 150 °C and different air pressures, the pH did not decrease from the initial value of 9.6 to <8.5, a value at which most of the sulfides are dissolved in water in the form of S²⁻ [47]. Thus, the elimination of these sulphur compounds by stripping in the form of acid gas is discarded. The elimination is through the oxidation to sulphates (SO₄²⁻) by the oxygen dissolved in the reaction medium with a stoichiometric consumption of 2 g O₂/g S²⁻ [50].

Likewise, at 150 °C, the organic matter removal in terms of the total organic carbon (TOC) was 6 %, 9 % and 14 % for operating air pressures of 10, 50 and 90 bar, respectively. The reduction in terms of COD was significantly higher (18 %, 27 % and 28 %) due to the simultaneous removal of sulfides previously mentioned, which have a contribution to COD. Despite the moderate removal of TOC and COD, the most abundant pollutant identified in the water, MDEA, was eliminated by 10 %,

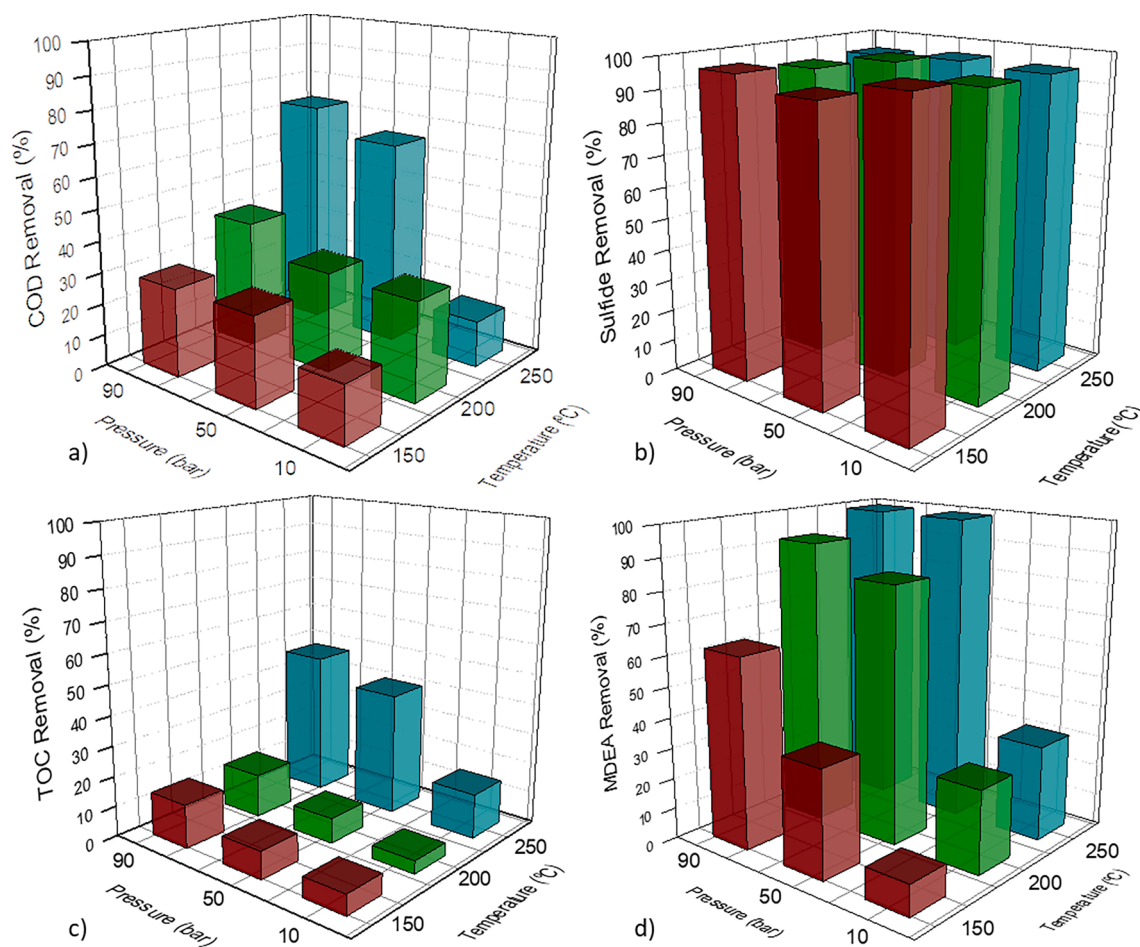


Fig. 2. Influence of the air pressure and temperature in the treatment of highly concentrated spent caustic wastewater. a) COD removal; b) sulfide removal; c) TOC removal and d) MDEA degradation.

35 % and 62 %. Therefore, at the temperature of 150 °C MDEA cannot be removed completely resulting in concentrations in the treated effluent that exceed 1,000 ppm even for 90 bar of air operation pressure, which is still too high for the downstream biological treatment, despite the dilution of this effluent by mixing with the rest of the wastewater streams coming from different refinery processes.

Therefore, in order to enhance the performance and taking into account the effect of the increase of pressure and temperature on the overall economy of the WAO process due to the rise in energy consumption, the reaction temperature was raised to 200 °C. The increase of 50 °C produced an enhanced in the amount of oxygen dissolved in the water (ca. 1.5 times for the same working air pressures [45,46]). The increase of temperature hardly enhanced the TOC removal, maintaining similar efficiencies to those obtained at 150 °C, whereas the COD removal increased, with reductions of 24 %, 32 % and 38 % for the air pressures of 10, 50 and 90 bar, respectively. In the case of MDEA removal, more than 80 % and 90 % were achieved at air pressures of 50 and 90 bar, leading to final concentrations of 497 and 177 ppm, respectively. In these cases, the dilution of this stream with the rest of the wastewater streams of the refinery would allow reaching MDEA concentration at which very limited effects on the biological process of the wastewater treatment plant are expected. The WAO process is therefore effective for the treatment of wastewater with high MDEA concentration at typical operation conditions of temperature (200 °C) and air operation pressure (up to 90 bar). The main pollutants of the wastewater, MDEA and sulfides, are removed without the need to achieve a high removal of organic matter.

At this point, the increase of temperature to 250 °C was also assessed

for further reduction of organic matter. The effect of temperature on the amount of dissolved oxygen in the reaction medium is increased by 1.7 times compared to the same working pressures and 200 °C [45,46]. At 250 °C and 50 or 90 bar air pressure, the elimination of MDEA was almost complete (99 %) and over 95 % for sulfides. In this case, the mineralization of organic carbon increases up to 40 %, with COD reductions of more than 65 %. A decrease in final pH of the wastewater occurs from the natural initial value of 9.6 to 4.8 because of the oxidation process. This acidic character can cause corrosion problems in the facilities needed for treatment [52] even having been established as a worldwide problem in sewers due to corrosion caused by H₂S in wastewater [53]. This decrease in pH is associated to the organic matter oxidation and conversion of sulfides to sulphates and sulfuric acid by the high pressure WAO process [54]. This acid partially consumes the alkalinity of the spent caustic from the wastewater. In addition, the organic matter contained in the water is oxidized to low molecular weight carboxylic acids that contribute to the acidity of the water. Among the distinct low molecular weight carboxylic acids, WAO process is characterized by promoting the formation of acetic acid as main oxidation by-product [44]. Acetic acid is quite difficult to further oxidize to carbon dioxide and water by WAO process, being necessary to use very extreme operating conditions or to work with catalysts that facilitate the process [55]. In this work, acetic acid concentrations higher than 400 ppm were detected in the wastewater after WAO treatment. This formation of carboxylic acids together with the oxidation of sulfides to sulphates, results in the consumption of alkalinity and consequent decrease in the pH of the water.

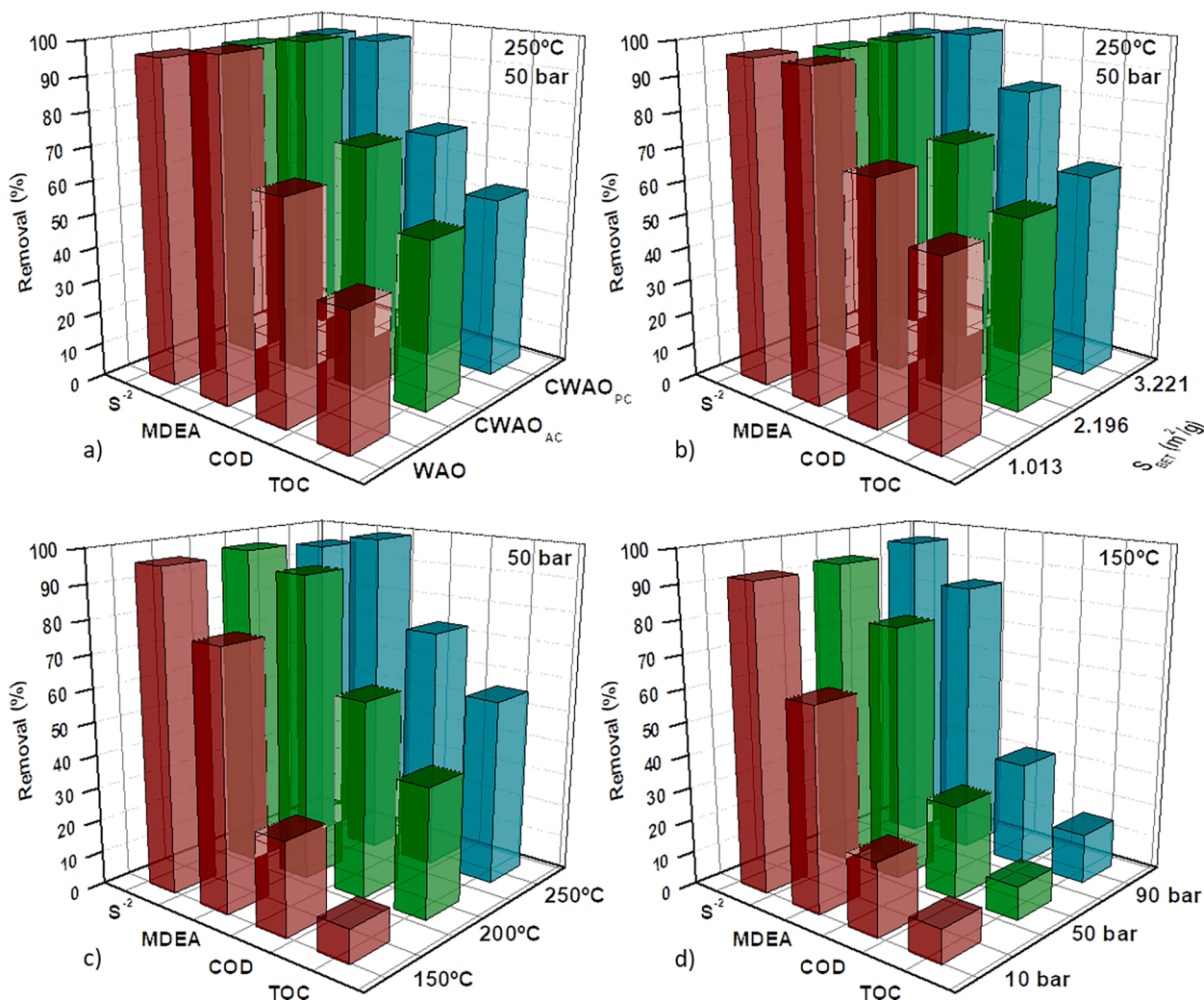


Fig. 3. Sulfide, MDEA, COD, TOC removals of catalytic carbonaceous material CWAO_{PC} 2,196 m²/g prepared from petcoke: a) 250 °C and 50 bar for WAO and CWAO process with commercial or synthesised catalyst (CWAO_{PC} 2,196 m²/g); b) CWAO at 250 °C and 50 bar for prepared catalysts of different specific surface areas; c) CWAO at 50 bar for different temperatures with prepared catalyst (CWAO_{PC} 2,196 m²/g) and d) CWAO at 150 °C for different air pressures with prepared catalyst (CWAO_{PC} 2,196 m²/g).

3.3.2. Catalytic activity of petcoke-based catalysts

Initially, operation conditions of 250 °C and 50 bar of air pressure were used for testing the catalytic performance of activated carbonaceous materials. Air pressure at 50 bar was used as the increase of air pressure above this value hardly improved the COD reduction and TOC mineralization for WAO experiments. In these conditions, the catalytic activity of commercial activated carbon (CWAO_{AC}) with a specific surface area of 1,288 m²/g and activated carbon materials from petcoke (CWAO_{PC}) with different specific surface areas (1,013 m²/g, 2,196 m²/g and 3,221 m²/g) was evaluated to compare its effect on oxidation yields (Fig. 3a and b). In general, non-significant differences were observed for the four carbonaceous materials and the non-catalytic WAO process at these operating conditions and 60 min of reaction for all the experiments. The commercial activated carbon achieves near-complete removal of MDEA and sulfides. A slight increase in the mineralization degree of the organic matter and reduction of COD was observed for the CWAO_{AC} compared to the WAO. The carbonaceous material synthesized from petcoke (CWAO_{PC} 2,196 m²/g) shows similar results to the commercial activated carbon, with amine and sulfide degradations of 99 % and 95 %, and TOC and COD reductions of 56 % and 76 %, respectively. These performances are maintained for the carbonaceous material with a lower specific surface area (CWAO_{PC} 1,013 m²/g) and the TOC and COD removals were slightly improved using the carbonaceous material

of the highest specific surface area (CWAO_{PC} 3,221 m²/g) and higher O/C ratio according to the SEM-EDX analyses (Fig. 5_{SM}).

In order to determine a higher influence of the catalyst compared to the non-catalytic WAO process, the air pressure and temperature were decreased to milder operating conditions. This study was carried out with the CWAO_{PC} 2,196 m²/g carbonaceous material prepared from petcoke as the most available catalyst of the three CWAO_{PC} materials and similar catalytic performance to commercial activated carbon (CWAO_{AC}).

The influence of temperature at constant air pressure of 50 bar and air pressure at constant temperature of 150 °C for the catalyst CWAO_{PC} of 2,196 m²/g is shown in Fig. 3c and 3d, respectively. The performance of CWAO at 50 bar when the temperature decreased from 250 °C to 150 °C evidenced a more remarkable difference between the results of CWAO and WAO experiments. The elimination of MDEA exceeds 90 % for the two upper temperatures of 200 °C and 250 °C, reaching a MDEA removal of 77 % at 150 °C (only 35 % for the WAO treatment). At lowest temperature, the catalyst proves a significant effect, increasing the removal of MDEA, the main pollutant in the actual refinery wastewater stream, by more than twofold. Concerning the removal of sulfides and the reduction in TOC and COD, a slight improvement was also observed in comparison to the results of the WAO process.

The effect of the air pressure for the CWAO in the range of 10 and 90

bar was also seen at the lowest temperature of 150 °C. At 10 bar, 61 % of the initial high concentration of MDEA in the wastewater (2,521 ppm) is removed, with the total oxidation of sulfides to sulphates. This is a 50 % improvement in amine degradation referred to the oxidation without catalyst. Increasing the pressure to the upper studied limit of 90 bar yields an MDEA removal of more than 80 % compared to 62 % obtained with the WAO process. Thus, the carbonaceous catalyst $\text{CWAOP}_{\text{C}} 2,196 \text{ m}^2/\text{g}$ improves the performance of the oxidation process. The functional groups of the catalyst promote the reduction of the oxygen in the medium, generating radicals of greater oxidizing power that can oxidize the compounds present in the wastewater [28]. The oxidation under these mild operation conditions with the catalyst results in a higher oxidation of the MDEA and organic compounds with a slight enhancement of COD and TOC removals.

Therefore, the catalytic material with high porosity and specific surface area prepared from petcoke proves to be an effective catalyst for the WAO process, improving the yields achieved under mild operating conditions. The CWAO process, which achieves high removals of MDEA and sulfides from the water under mild operating conditions, will probably improve the biodegradability of the wastewater. This is also an important factor in terms of the performance of the centralized biological treatment system of the refinery's wastewater treatment plant. Despite this, the actual biodegradability of the oxidation products generated in the WAO and CWAO processes needs to be studied. This would allow establishing the real effect of the effluent generated in the process on the biological treatment system, as well as the optimal operating conditions at which the pretreatment of the stream with high MDEA should be carried out.

3.3.3. Oxidation products from WAO and CWAO of methyldiethanolamine (MDEA)

Most of the studies of WAO for wastewater treatment are mainly focused on quantifying the degradation of the organic matter in terms of COD and TOC reductions. However, it is essential to identify oxidation by-products or intermediates from nitrogen-containing organic compounds to evaluate their potential toxicity and/or refractory behavior for subsequent biological treatment. The WAO of nitrogen-containing compounds can produce different products including ammonium, nitrate, nitrite, nitrous oxide and nitrogen gas depending on the pollutant and reaction conditions [21–23]. When the main nitrogen input is an amine-containing compound, ammonium is mainly produced as stable end-product at harsh oxidation conditions [51].

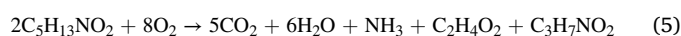
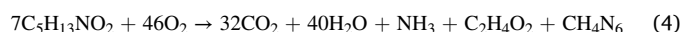
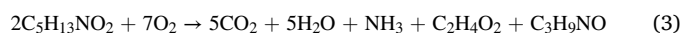
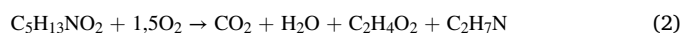
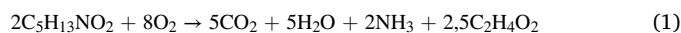
Fig. 4 shows the concentration of nitrogen-containing compounds in the wastewater such as the MDEA itself, other nitrogen organic products and inorganic nitrogen as ammonium and nitrates/nitrites, for the WAO and CWAO treated waters after 60 min under different operation conditions. The initial MDEA concentration (2,521 ppm) is about 300 ppm in terms of nitrogen content and contributes to ca. 95 % of the total nitrogen of the wastewater. WAO experiments at 150 °C evidenced a low formation of inorganic nitrogen compounds. MDEA and nitrogen-containing organic by-products were the most abundant compounds. The contribution of MDEA was up to ca. 50 % for the highest air pressure. The increase of temperature at 200 °C resulted in the elimination of MDEA of 27 %, 83 % and 95 % for the 10, 50 and 90 bar, respectively. The increase of air pressure led to 10 % of inorganic nitrogen such as $\text{NO}_3^-/\text{NO}_2^-$. At the highest temperature (250 °C), the increase of air pressure enhanced the inorganic nitrogen products up to 40 %, out of which 30 % corresponding to ammonium.

The use of the carbonaceous material synthesized from petcoke as a catalyst ($\text{CWAOP}_{\text{C}} 2,196 \text{ m}^2/\text{g}$) shows a higher contribution of non-identified organic nitrogen compounds at low temperature (150 °C) and different air pressures in comparison to the analogous WAO experiments, and the oxidation to $\text{NO}_3^-/\text{NO}_2^-$ and ammonium was hardly detected. As the temperature was increased up to 250 °C at 50 bar, the oxidation of the nitrogen organic compounds led to ammonium contents higher than those observed in WAO experiments at the analogous

operation conditions, and low presence of $\text{NO}_3^-/\text{NO}_2^-$. Thus, the increase in temperature and air pressure using the carbonaceous activated carbon as catalyst for CWAO, decreased the MDEA contribution to the total nitrogen content promoting the generation of ammonium as main inorganic nitrogen by-product. Ammonium obtained as a product of MDEA oxidation has a certain refractory character to the WAO and CWAO processes, resulting in low elimination in the form of nitrogen gas [23] as also attested from the negligible decrease of total nitrogen. Nevertheless, ammonium can be consumed as a nutrient by aerobic biological treatment systems [56].

As shown in Fig. 4, the contribution of non-identified organic nitrogen compounds stemming from the partial oxidation of MDEA (termed as “other organic” in the graph) to total nitrogen varies depending on the operation conditions of WAO and CWAO. The oxidation of MDEA follows a very complex mechanism with a large number of by-products whose formation has not been explained in many cases [13,20,22,23,57–59]. As other amines, MDEA is oxidized to organic acids and glycine as main by-products, but unspecified formyl-amides have also been reported as secondary by-products [57]. Formation of diethylamine (DEA), *N*-methylamine (MMA), or ethanolamine (MEA) may occur concurrently with a methyl group transfer from MDEA or by direct oxidation. These compounds may react with other compounds formed in the oxidation process of MDEA, leading to a chain of reactions that are difficult to define [57]. In the CWAO, the degradation of MDEA using metal-free carbon catalysts has been demonstrated to be strongly dependent on the chemical surface groups of the materials, which play a key role in the production of active oxidizing species. Thus, it is well recognized that the adsorption of O_2 over the carboxyl groups of activated carbon surface produces its dissociation to form $\cdot\text{O}_2$ species [60]. Then, hydroxyl radicals ($\cdot\text{OH}$) are generated by electron transfer of $\cdot\text{O}_2$ or attracting H^+ of the carboxyl groups. In addition, the basic groups of the activated carbon surface have also an important role attracting small molecules of carboxylic acids, which can react with $\cdot\text{OH}$ to generate CO_2 and H_2O . In the case of MDEA, the hydroxyl radicals can also attack the C–N bond of the MDEA to generate other intermediate products which will be oxidized to carboxylic acids, ammonium, CO_2 and H_2O [27]. In this study, the analysis of the oxidation products of the treated wastewater under the different operating conditions has resulted in the detection of acetic acid, ammonium, and other by-products of the oxidation of MDEA such as dimethylamine, tetrazole-1,5-diamine, 2-amino-1-propanol, and alanine among others.

Acetic acid appeared in all the oxidation reactions (WAO and CWAO), being its contribution over the total organic carbon more important as temperature and air pressure is increased or when catalyst was used (Fig. 6 SM of SI). The rest of the identified compounds varied without a clear trend. Fig. 5 shows the potential oxidation reactions of MDEA based on the products identified for the different operating conditions of WAO and CWAO. In these reactions, water and carbon dioxide are also produced because of the mineralization of organic matter as deduced from the reduction of the TOC and COD of the wastewater.



The complex nature of the petrochemical wastewater and the variety of generated by-products makes necessary to analyze the actual biodegradability of the effluents after the WAO or CWAO treatment. The generation of acetic acid and ammonium as main products of the oxidation process suggests a potentially increased biodegradability of the effluent, which should be easily treated in the conventional

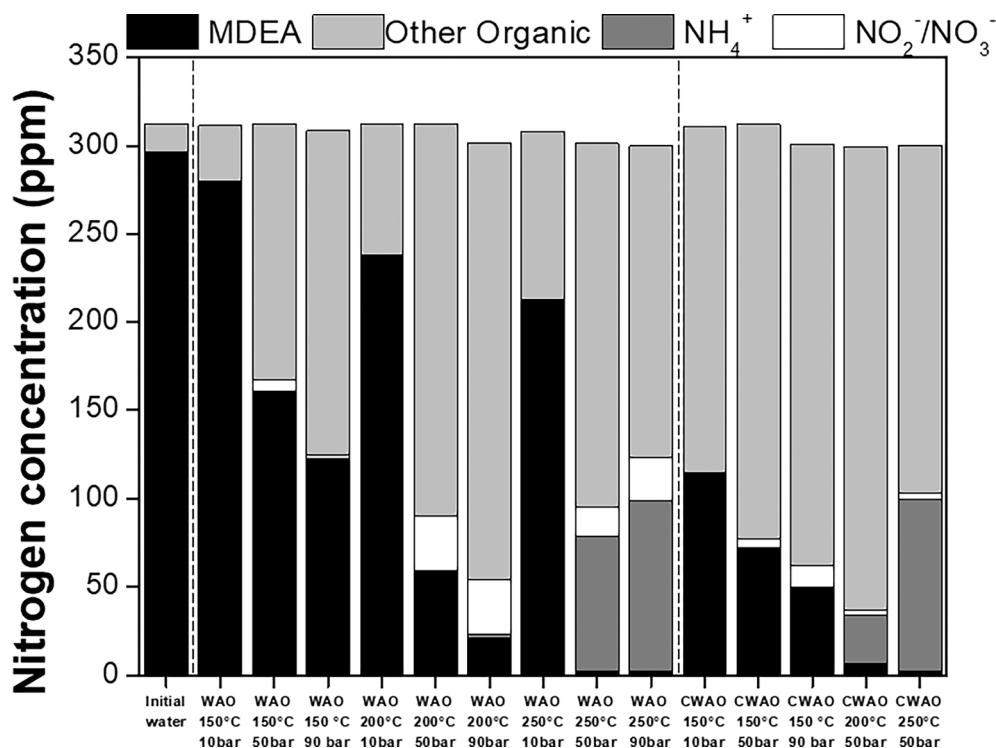


Fig. 4. Influence of the oxidation conditions of WAO and CWAO on the contribution of nitrogen-containing compounds.

biological treatment system of the refinery's water treatment plant [3,56].

3.3.4. Biodegradability of WAO and CWAO-treated wastewater effluents

To evaluate the rapid biodegradability of the treated effluents obtained in different oxidation conditions of WAO and CWAO runs, respirometric tests were performed with an activated sludge culture acclimatised for months to sodium acetate as biodegradable substrate. The toxicity and inhibition effects of the treated effluents on the readily biodegradable substrate were also assessed using the classical respirometric bioassays [35], but no conclusive results could be obtained. The spent caustic wastewater, containing 2,521 ppm of MDEA, high COD, TOC and sulfides, evidenced a low biodegradability of ca. 4 % compared to the sodium acetate solution used as a readily biodegradable substrate.

Fig. 6a depicts the compositional percentage of MDEA and acetic acid (both relative to TOC), and ammonium relative to Total Nitrogen (TN) in relation to the biodegradability of the treated effluents. Fig. 6b shows the results of biodegradability of treated wastewaters at 150, 200 and 250 °C using 50 and 90 bar air pressure for WAO and the same temperatures using 50 bar for CWAO (activated carbon material prepared from petcoke with specific surface area of 2,196 m²/g).

The samples of WAO treatment showed a remarkable increase of biodegradability at 250 °C (ca. 50 %) as compared to the results at 200 °C (ca. 20 %), regardless the applied air pressure (50 or 90 bar). This fact is attributed to the absence of MDEA and higher contribution of acetic acid in the remaining TOC of the sample for 250 °C. Moreover, the percentage of ammonium respect to the TN was also much higher at 250 °C, which is decreasing the amount of other nitrogenated organic by-products, presumably with lower biodegradability. At 150 °C, the presence of MDEA in significant amounts and presence of less biodegradable nitrogenated organic compounds, leads to a dramatical decrease of biodegradability (<5 %). In contrast, the CWAO significantly increases the biodegradability at the three studied temperatures using 50 bar of air pressure. At 250 °C, the high content of acetic acid and ammonium are probably boosting the increase of biodegradability up to almost 70 %. At lower temperatures, 200 and 150 °C, the

biodegradability decreased up to ca. 30 % and 25 %, respectively, due to remaining amounts of MDEA and lower contents of ammonium, but these values are much higher than those obtained in WAO at the same operation conditions.

The fact that the biodegradability cannot reach values close to 100 % is attributed to the presence of nitrogenated organic compounds produced by the oxidation of MDEA, which may require longer degradation times than those established in the respirometric tests. It should be noted that these tests show the biodegradability of the effluents generated in short periods of time, for an activated sludge acclimatized to a model substrate [35]. The performance of an activated sludge process in refinery's wastewater treatment plant should be better, leading to a higher biodegradability of the effluents of the WAO and CWAO processes. These treatment plants have activated sludge systems acclimatized to less biodegradable compounds, with a higher concentration of active biomass than that used in these respirometric tests and operating at higher hydraulic residence times [3,4]. In addition to the improvement expected from operation at the refinery's wastewater treatment plant, biodegradability achieved by WAO and CWAO treatment of the spent caustic stream at the outlet of the unit, where the pollutant load is the highest, makes it viable for the effluent to reach the biological treatment system after dilution with other wastewater streams generated in the refinery. This would further reduce the pollutant load reaching the treatment system making treatment even easier.

4. Conclusions

The WAO process is an effective treatment of the refinery spent caustic stream with high MDEA contamination from amine absorption units in the purification of refinery gas streams. A deep study of the operating conditions has been performed as MDEA is a tertiary amine that can cause significant problems in the centralized biological system of the refinery's wastewater treatment plant. The experiments were performed at the original pH of the wastewater despite its high alkalinity, which assure that sulfides are removed by oxidation to sulphates and using air instead of pure oxygen as source of oxidising agent. The

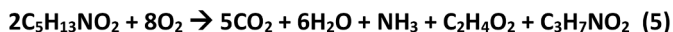
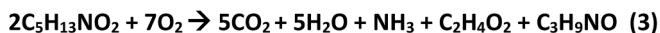
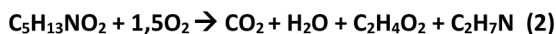
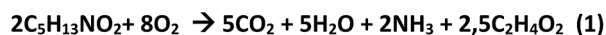
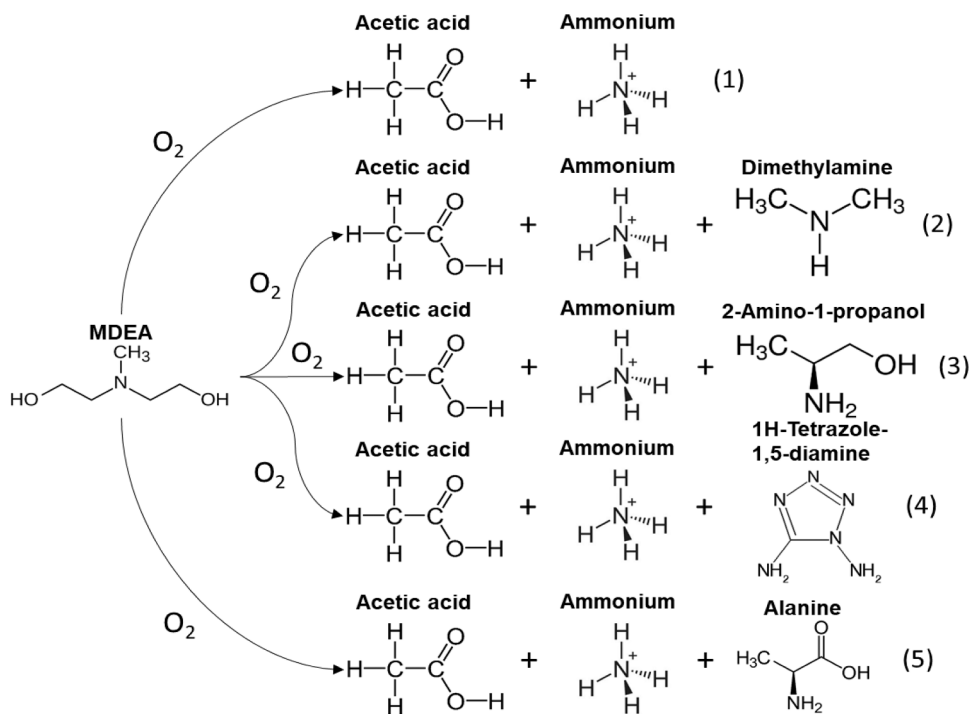


Fig. 5. Potential oxidation reactions in the treatment of highly MDEA concentrated wastewater.

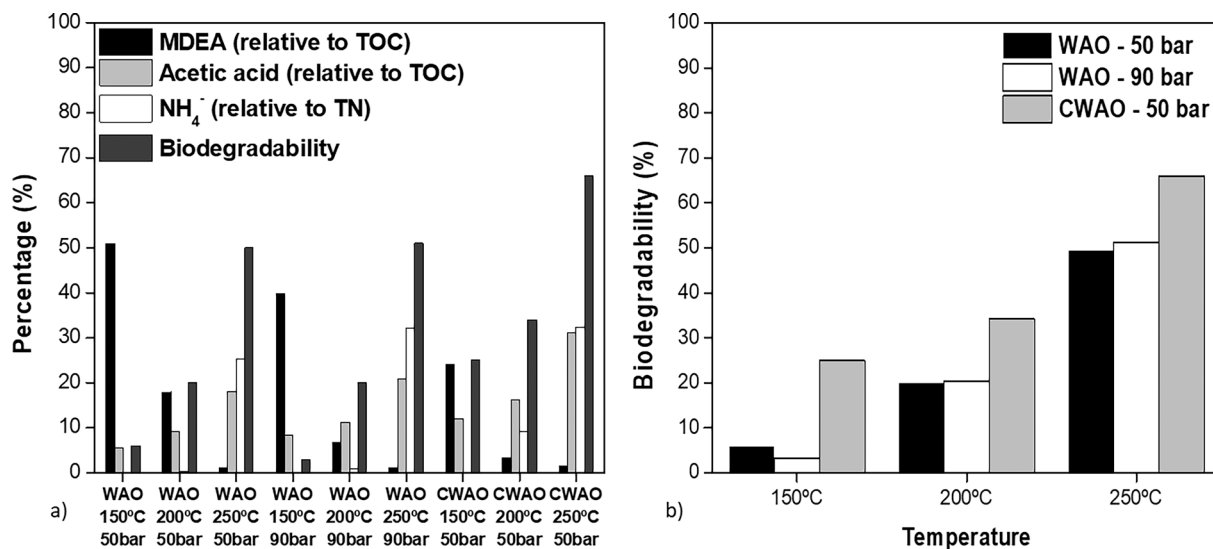


Fig. 6. Percentage of MDEA and acetic acid (relative to TOC), ammonium (relative to TN) and TOC (a) and biodegradability (b) of treated wastewaters at different oxidation conditions WAO and CWAO (activated carbon material prepared from petcoke with specific surface area of 2,196 m²/g).

increase of temperature has a more important effect than the air pressure on the performance of the treatment in terms of the reduction of MDEA, sulfides, COD and TOC. The WAO at 250 °C or even 200 °C at 50 bar of air pressure can be considered an effective technology for the *on-site* treatment of highly MDEA concentrated wastewater. Under these conditions, more biodegradable streams enriched in acetic acid and ammonium compounds were achieved, although their biodegradability could not overpass ca. the 50 %. On the other hand, microporous carbonaceous materials prepared from a refinery petcoke by chemical activation under different conditions were tested as catalysts in CWAO. These materials showed high specific surfaces areas ranging between 1,013 and 3,459 m²/g. A carbonaceous material prepared in this work with a specific surface area of 2,196 m²/g proved a better performance at milder operation conditions than WAO experiments using the same operation conditions. The MDEA removal was improved by more than twofold at 150 °C and 50 bar of air pressure. At 250 °C, the CWAO was able to achieve an increase of biodegradability up to 70 %. The biodegradability decreased up to ca. 30 and 25 % at 200 °C and 150 °C, respectively. But these values were still significantly higher than those obtained for WAO experiments in analogous operation conditions (20 % and < 5 %). It must be noted that these results of biodegradability were estimated according to respirometric tests, whereas biological treatment of the refinery's wastewater treatment plant would operate with a more acclimatized activated sludge and long hydraulic residence times, which can overcome potential problems caused by the presence of remaining MDEA and nitrogenated by-products. In this sense, a compromise between the operating conditions and the resultant biodegradability of the effluent for subsequent mixture with other refinery wastewaters is needed to reduce the operational expenditure of WAO and/or CWAO and determine the techno-economic feasibility of the industrial implementation of this technology as a pre-treatment step for the highly MDEA concentrated wastewater streams.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2023.141692>.

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