Research article

Carbonaceous materials from a petrol primary oily sludge: Synthesis and catalytic performance in the wet air oxidation of a spent caustic effluent

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ABSTRACT

Oil refineries produce annually large quantities of oily sludge and non-biodegradable wastewater during petroleum refining that require adequate management to minimize its environmental impact. The fraction solid of the oily sludge accounts for 25 wt% and without treatment for their valorization. This work is focused on the valorization of these solid particles through their transformation into porous materials with enhanced properties and with potential application in the catalytic wet air oxidation (CWAO) of a non-biodegradable spent caustic refinery wastewater. Hence, dealing with the valorization and treatment of both refinery wastes in a circular approach aligned with the petrol refinery transformations by 2050.

The obtained oily sludge carbonaceous materials showed improved surface area (260–762 m^2/g) and a high Fe content. The good catalytic performance of these materials in CWAO processes has been attributed to the simultaneous presence of surface basic sites and iron species. Those materials with higher content of Fe and basic sites yielded the highest degradation of organic compounds present in the spent caustic refinery wastewater. In particular, the best-performing material ACT-NP 1.1 (non-preoxidated and thermally treated with 1:1 mass ratio KOH:solid) showed a chemical oxygen demand (COD) removal of 60 % after 3 h of reaction and with a higher degradation rate than that achieved with thermal oxidation without catalyst (WAO) and that using an iron-free commercial activated carbon. Moreover, the biodegradability of the treated wastewater increased up to 80% (from ca. 31% initially of the untreated effluent). Finally, this material was reused up to three catalytic cycles without losing metal species and keeping the catalytic performance.

1. Introduction

Petroleum industries are currently facing a significant challenge to reduce the amount of waste generated during the petroleum refining processes. Refinery wastewater and oily sludge are the main wastes produced, which present a toxic composition due to the presence of petroleum hydrocarbons (PHCs), recalcitrant compounds, and volatile organic compounds (VOCs). The release of these compounds creates serious environmental concerns, such as soil, groundwater and air pollution (Hui et al., 2020; Jasmine and Mukherji, 2015; Li et al., 2020). So, they must be appropriately handled and disposed of, which usually supposes high costs for the refinery plant (Jerez et al., 2023).

The generation of hazardous refinery sludges is estimated at 310,000 tons in the EU annually (Jerez et al., 2023). Usually, oily sludge is a complex and stable oil/water emulsion composed of three different phases: oil (15–50 wt%), water (30–85 wt%) and solid particles (5–46 wt%) (Jerez et al., 2021). This waste contains high concentrations of petroleum hydrocarbons (PHCs) and other toxic substances like chemical additives and heavy metals (Fe, Cu, or Ni) (X. Li et al., 2020; Jun Wang et al., 2017). Thus, the adequate management of this waste is crucial to meet current EU legislation (Eurpoean Comission, 2020).

The conventional treatments applied to date allow the recycling of the oil fraction (solvent extraction, centrifugation, etc.) (Hu et al., 2013; Hui et al., 2020; Johnson and Affam, 2019), and the aqueous phase is usually recirculated to the wastewater line process. Therefore, the main problem is managing the remaining solid particles, which represent a high amount of the total waste.

According to the strategies for the 2050 refineries, the valorization of

waste materials is proposed as a new alternative to achieving a new concept of the refinery industry. However, further technology development is required to adapt waste processing streams to produce feedstock that can be used in a refinery to obtain products with quality (Fuels Europe, 2018). Because of that, incentives for the use of waste in refining processes are taking most importance. Especially those refinery wastes that could be reused in the plant, creating a process linked with the EU Circular Economy Action Plan.

The synthesis of activated carbon from carbonaceous residues has attracted particular attention, over the past few years (Yang et al., 2019). Several authors have investigated the synthesis of carbonaceous materials from different derived waste feedstock. In these works (Abuelnoor et al., 2021; Bernardo et al., 2021; Marcuzzo et al., 2014; Monsalvo et al., 2011; Nicolae et al., 2021; Spessato et al., 2019; Wen et al., 2011), other wastes, such as biomass or sewage sludge, are thermally and/or chemically activated to yield porous materials with enhanced textural properties and surface area. These new materials have been tested as adsorbents of wastewater and gas streams such as ammonia or CO_2. However, the use of these new materials could not be implemented in the same industry as the feedstock, so it does not allow the creation of a circular process, which is a principal aim of this study. Likewise, the synthesis of carbonaceous materials from refinery wastes has been investigated by several authors (Andrade et al., 2009; Fan et al., 2022; Li et al., 2017; Liu et al., 2022; Mohammadi and Mirghaffari, 2015; Wang et al., 2017). These previous works reported the feasibility to synthetized oily-sludge based materials with improved textural and chemical properties, which can be used as adsorbents or semiconductors. However, none of these works have studied the catalytic application of these materials. And they have mainly downplayed the importance of the solid fraction of refinery sludge. This difference is essential due to the current problems in the refinery plant to properly manage oily sludge. Recent work by this group reports on the situation and proposes new sustainable strategies through fractional valorization of oily sludge (Jerez et al., 2021, 2023), with the solid phase needing further development for its valorization.

The oily sludge-solid particles typically present high C content, as well as metals, principally Fe (39 wt%) (Jerez et al., 2021), which are crucial parameters to obtain materials with enhanced textural properties by a combination of thermal and chemical activation processes (Guritno et al., 2016). This allows to propose its application in some catalytic reactions. Wet air oxidation (WAO) is a well-known technology, commonly applied to industrial wastewater for the removal of refractory organic compounds using high temperature (200–300 °C) and air pressure (30–70 bar). The efficiency of this process increases with the presence of a catalyst (CWAO), allowing it to work under milder conditions (Kim and Ihm, 2011; Rocha et al., 2020). Several authors have investigated this technology (Aguilar et al., 2003; Quintanilla et al., 2010; Rocha et al., 2020; Wang et al., 2014). These authors reported an improvement in the CWAO process for wastewater treatment, using different catalysts such as activated carbons, noble metals catalysts, or functionalized carbon materials. Emphasising the importance of their chemical and textural properties, which can be improved by thermochemical processes.

Marques et al. synthetized new materials from sewage sludge with surface areas up to 864 m^2/g and good catalytic activity in the oxidation of phenol, which is correlated to their high content of active metals (especially Fe) (Marques et al., 2011). Similar applications have been investigated by de Mora et al. producing sludge-based materials with good performance as catalysts for wastewater treatment. Noting the importance of metal content to improve the catalytic performance in the CWAO process (de Mora et al., 2024).

However, to the best of our knowledge, this work is the first study that investigate catalytic applications for oily sludge-based materials and specifically uses it in CWAO reaction for refinery wastewater treatment. A recent work of our research group has demonstrated that active carbon-based catalysts from refinery petcoke can be used as catalysts for the treatment of refinery wastewaters, in terms of chemical oxygen demand (COD) and total organic carbon (TOC) removal (González et al., 2023). Based in these results, we wanted to go a step forward and develop new synthesis methodology to achieve the valorization of the solid fraction of oily sludge into new carbonaceous materials, and their catalytic application in CWAO treatment of a refinery wastewater, creating a circularity process in the refinery plant.

Therefore, the aim of this study is to settle the best conditions for the synthesis of porous carbonaceous materials using the solid fraction from oily sludge as well as to study its performance in the CWAO process of a spent caustic refinery wastewater. In consequence, this strategy allows the valorization and treatment of both refinery residues in a circular approach, within the framework of the EU petrol refinery's transformations for 2050 (Gudde et al., 2019).

2. Materials and methods

2.1. Source of oily sludge and spent caustic wastewater

The oily sludge used in this study comes from an API separator of a wastewater refinery treatment plant (WWTP). The refinery wastewater is an amine-contaminated, spent caustic refinery effluent. Both residues were collected from a petroleum refinery plant located in Spain. Samples were collected and immediately stored at 4 °C to keep in unchanged conditions.

2.2. Main physicochemical properties of oily sludge and spent caustic wastewater

Oily sludge consists of three phases, where the relative content was 34, 41, and 25 wt% for oily, aqueous, and solid phases, respectively. The characterization of this oily sludge was exhaustively carried out in a previous work of this group (Jerez et al., 2021). The refinery wastewater (spent caustic effluent) comes from an amine unit in a petroleum refinery in Spain. This effluent presents a low solids concentration (<40 mg/L), a basic pH (10.0 ± 0.1) and a high concentration of tCOD (5.0 ± 0.2 g/L) and TOC (1.4 ± 0.4 g/L), as well as low biodegradability (31%) according to respirometric assay, which makes unfeasible its treatment through conventional biological processes. Methyldiethanolamine (MDEA) is the most abundant compound present in refinery wastewater with a concentration ca. 2.5 g/L. However, the concentration of metals is low (Ca, Si and Mg < 5 ppm) as reported by González et al. (2023).

2.3. Analytical methods

2.3.1. Oily sludge and spent caustic wastewater characterization

pH was measured using a GLP-22 digital pH meter (HACH LANGE SPAIN, S.L.U). Total Chemical Oxygen Demand (TCOD) was measured following an optimized method for samples with a high content of solids published by Raposo et al. (2008). Soluble Chemical Oxygen Demand (SCOD), and the total solid content were measured following APHA-AWWA Standard methods 5220.D and 2540.B, respectively (APHA-AWWA-WEF, 2005). For the aqueous phases, Total Organic Carbon (TOC) was measured using a combustion/nondispersive infrared gas analyser model TOC-V CSH (Shimadzu), while Ammonia (NH_4^+) and phosphate (PO_4^{3-}) concentration dissolved were determined using Smartchem 140 (AMS Alliance), following APHA-AWWA Standard methods 4500-NO2 B and 4500- P E, respectively (APHA-AWWA-WEF, 2005). The content of metal elements in the aqueous phase was measured with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) using a Varian Vista AX spectrometer.

2.3.2. Synthetized carbonaceous materials characterization

Elemental analysis (CHNS) was carried out by an analyzer Flash 2000 (Thermo Fisher Scientific, Massachusetts, USA) equipped with a thermal conductivity detector (TCD). The content of metals was

analyzed by X-ray fluorescence (XRF) in a spectrometer Philips MagiX. Oxygen content (O) was determined by mass balance, considering the elemental composition and the metal content determined by XRF.

Nitrogen adsorption isotherms were determined using a Micro Active for Tristar II Plus (Micromeritics). The samples were outgassed using a heating rate of 5 °C/min until 90 °C for 30 min and then by another heating rate of 5 °C/min until 150 °C for 480 min. The specific surface area was calculated by the Brunauer-Emmett-Teller method (S_{BET}). The total pore volume was defined as the net amount of nitrogen adsorbed to the $P/P_o = 0.99$, whereas the micropore and mesopore volume and surface areas were calculated using the t-plot method.

The morphologies and microscopic composition of the materials were analyzed by scanning electronic microscopy (SEM) using a Phenom XL G2 Desktop SEM equipped with energy-dispersive X-ray spectroscopy (EDX). The crystallographic analysis was carried out by powder X-ray diffraction (XRD) with a Philips X-Pert diffractometer using Cu Kα radiation. The data were recorded in the 2θ range from 5 to 90°. X-ray photoelectron spectroscopy (XPS) was acquired with a Physical Electronics spectrometer model PHI 5701, to analyze the surface characteristics of the carbonaceous materials. The analysis was performed using X-ray source with Al and Mg anodes. Concentric hemispherical analyzer operating in the constant pass energy mode at 29.35 eV, using 400 μm diameter analysis area.

Boehm titrations were carried out to determine the presence of basic surface functional groups. These determinations were carried out using 0.15 g of the sample, which is in contact with HCl 0,05M for 24h. The titration was carried out using NaOH 0,05M until a neutral pH was reached (Fidel and Thompson, 2013).

2.3.3. Biodegradability assessment of wastewater effluents

The biodegradability tests were performed at room temperature in a LFS (liquid-flow-static) respirometer consisting of a magnetically stirred vessel of 1 L of capacity inoculated with aerobic biomass (927 ± 1 mg VSS/L) taken from an urban wastewater treatment plant located at Toledo (Spain). Aeration was supplied through an air pump and a micro-diffuser at a continuous airflow of 0.46 L/min. The temperature was controlled at 25 °C with a thermostatic bath, and pH was maintained at 7.5. The pH and dissolved oxygen (DO) were measured with a WTW-Sentix 81 and a WTW- CellOx 325 probes, respectively. Detailed information about the procedure was reported by Vasiliadou et al. (2018), where a comprehensive description of the methodology for calculating the percentage of biodegradability is clearly outline. Biodegradability tests were conducted to assess the impact of refinery wastewater on acclimated and controlled biomass cultures, following the experimental procedure reported by Vasiliadou et al. (2018). For this purpose, oxygen consumption and oxygen uptake rates were measured in response to various pulses of treated wastewater and sodium acetate as readily biodegradable control. After several months of acclimation to a sodium acetate-rich feed, which served as a readily biodegradable substrate for the biomass sourced from a local wastewater treatment plant, these tests were performed.

2.4. Synthesis of carbonaceous materials

The solid fraction of the oily sludge was used for the synthesis of new carbonaceous materials. This solid fraction present in the oily sludge was isolated, firstly drying at 80 °C overnight and then using diethyl ether as solvent to remove the oil content following the procedure reported in a previous work of this group (Jerez et al., 2021). Then it was activated as described below.

Carbonaceous materials were synthesized following the methodology described by previous authors (Wang et al., 2017). The mass ratio of KOH (purity ≥85%, LabKem) and the solid particles from oily sludge (ratio KOH: solid), as well as the absence or presence of the pre-oxidation step have been studied as key parameters. The synthesis protocol involves three thermal steps: pre-oxidation (under static air

atmosphere) at 420 °C for 120 min with a heating rate of 2 °C/min; mixing the solid with KOH as an activating agent and carbonization at 400 °C for 30 min in a flow N₂ atmosphere (heating rate of 4 °C/min); activation step (850 °C for 80 min) in a flow N₂ atmosphere with a 4 °C/min of heating rate; finally washing with distilled water up to neutral pH and final drying at 100 °C overnight. The KOH to solid mass ratio ranged from 0:1 to 3:1. A set of materials was also synthesized, omitting the initial pre-oxidation step. Accordingly, samples were named ACT-P 0.1 to 3.1 (with pre-oxidation) and ACT-NP 0.1 to 3.1 (without pre-oxidation), where numbers indicate the KOH to solid mass ratio. The synthesis was carried out using a tubular furnace ST-115020-PAD P (Forns Hobersal S.L) equipped with quartz tubes.

2.5. CWAO experiments: catalytic assessment of synthesized materials

CWAO reactions were carried out using a stirred stainless-steel autoclave reactor with 500 mL of capacity (model 4575A manufactured by the Parr Instrument Company, USA). The reactor was equipped with a turbine stirrer and an electrically heated jacket controlled by a Parr 4842 controller. The reactions were performed using 200 mL of the spent caustic wastewater (without any dilution), setting the temperature at 200 °C and 50 bar of initial pressure of air using a compressor (model CBA 6 EM, Champion) to generate an oxidative atmosphere using a gas inlet located on the top of the reaction vessel (González et al., 2023). The autogenous pressure achieved for all the reactions was 80 bar under the working temperature. The catalyst concentration was 1 g/L. Catalyst performance was assessed by monitoring chemical oxygen demand (COD) removal with the reaction time. The samples were collected through a dip tube immersed in the reaction mixture. The leaching of metal species within the aqueous phase was also measured for all the catalytic experiments to settle the catalyst stability.

Two additional blank experiments were also carried out. A WAO reaction without the addition of a catalyst (thermal oxidation) and a CWAO reaction using directly (without activating treatment) the raw solid fraction isolated from the oily sludge (CWAO 0). Moreover, to compare a metal-free activated carbon sample with a high surface area (ca. 1000 m²/g), an activated carbon NORIT GAC 830 W was used (CWAO NORIT).

Finally, the best catalysts were tested in several catalytic cycles. After the reaction, the catalysts were washed thoroughly with water and dried at 100 °C overnight. Then, these materials were re-evaluated under the same reaction conditions.

3. Results and discussion

3.1. Synthesis and characterization of carbonaceous materials

The raw solid particles used as feedstock in this work were isolated from the oily sludge following the methodology described by Jerez et al. (2021). These materials were comprehensively characterized to determine their main composition. Table S1 (available in supplementary material) summarizes the main features of the solid particles, evidencing that this feedstock is an organic-inorganic composite material with high C content (45 wt %), metals (34 wt %) and poor textural properties, which might limit its use in prospective catalytic applications (Jerez et al., 2021). Fe is the principal metal of these solid particles, representing a 15 wt % of the total metal content. The content of each other metals (Ni, Mg, Cr, among others) are also indicated but represent a much lower content, under 2 wt %.

In order to enhance the textural properties, different carbonaceous materials have been prepared using a modified method described by Wang et al., 2017, who have synthesized materials from oily sludge, studying the effect of oil content. It is well known the critical effect that the chemical activation with KOH has on the textural properties of activated carbon materials (Goel et al., 2021; Monsalvo et al., 2011; Wang et al., 2008). Hence, the KOH to solid oily-sludge mass ratio from

0:1 to 3:1 has been studied. Likewise, since the raw material is a composite of different metals and carbon particles, a preliminary oxidation step might be another key parameter to generate an active surface on the catalyst for oxidation reactions, which means metal oxide generation porosity and basic sites. Therefore, two different sets of materials were synthesized, one with a pre-oxidation step (ACT-P) and the other in the absence of this oxidative step (ACT-NP). Specific surface area (S_{BET}) and increasing porosity were used as control parameters to elucidate the best synthesis conditions (all the experiments were performed in triplicate).

Fig. S1 (a) (available in supplementary material) shows the adsorption-desorption nitrogen isotherms for the set of ACT-P solids using different mass ratios of KOH. According to the IUPAC classification, the materials exhibit a distorted combined type I/IV isotherms, indicating micropores and mesopores existence (Li et al., 2017; Lowell et al., 2004; Mohammadi and Mirghaffari, 2015). Hence, the synthesized material combines micro and mesoporous structures, likely caused by the mixture of carbonaceous and metal particles inherent to the samples. Similar results have been published by different authors after thermochemical activation of petrol refinery sludges (Guritno et al., 2016; Mohammadi and Mirghaffari, 2015; Wang et al., 2017).

Table 1 summarizes the total pore volume (V_T) and specific surface area (S_{BET}) as well as micropore ($V\mu$) and mesopore volume (V_m) of porous carbons obtained from oily sludge-solid particles. The effect of KOH is evidenced by a gradual V_T and S_{BET} increment for the ACT-P set of materials. In contrast, there is no obvious correlation with the evolution of microporosity and mesoporosity. The microporosity grew significantly with the impregnation with KOH at 1:1 mass ratio, rising from 0.024 cm^3/g to 0.19 cm^3/g. This corresponds to an increase in microporosity percentage from 25 % to 74 % of the total volume. However, higher KOH results in microporosity percentage values of ca. 30 %. Goel et al. (2021), reported that KOH enhances surface area and porosity by breaking down the carbon structure, acting as a catalyst to promote carbon oxidation. Likely, the combined effects of a higher KOH ratio and the pre-oxidation step leads to greater carbon loss and the collapse of the material matrix, thereby decreasing microporosity.

A parallel set of materials, omitting the pre-oxidation step, was addressed to simplify the synthesis protocol and minimize the potential oxidative loss of carbon species (ACT-NP). Fig. S1 (b) (available in supplementary material) shows the nitrogen adsorption-desorption isotherms of the ACT-NP materials for the different mass ratios of KOH. A similar adsorptive behavior is observed to that obtained for ACT-P materials combining type I/IV isotherms, but with significant differences in the textural properties (S_{BET} and V_T) (Table 1). The effect of the activating agent is more significant for this set of materials, achieving specific surface areas up to ca. 600 m^2/g and V_T up to 0.5 cm^3/g with the minimum content of the activating agent (ACT-NP 1.1). Similar trend has been reported by other authors, which indicates the necessity of a thermochemical treatment with KOH to enhance the textural properties, achieving 323 m^2/g of surface area, with a KOH mass ratio of 2:1 for an industrial sludge (Mohammadi and Mirghaffari, 2015), or up to 1002 m^2/g for paper mill sludge with a KOH mass ratio of

1:1 (Kang et al., 2006). Thus, the mass ratio of KOH has been reported as having an important role in creating porosity in these carbonaceous materials.

As the porous structure is mainly ascribed to the carbonaceous part of the material, the pre-oxidation step partially destroys carbon species, thus decreasing textural properties. The pore development occurs in four stages: (i) opening of previously inaccessibly pores, (ii) creation of new pores, (iii) widening of the existing pores, and (iv) merger of the existing pores due to the pore wall breakage, being this mechanism easier for the carbonaceous phase rather than for the complex mixture of metals (inorganic phase) (Rodriguez-Reinoso, 1991). It is noticeable that in these materials, higher KOH loading induces higher S_{BET} and V_T in contrast with the results obtained for the oxidized materials. Hence, keeping in mind that the partial carbonaceous nature of the raw material would be responsible for the enhancement of the porosity after the thermochemical treatment. Montes and Hill (2018), reported an enlargement of mesoporous volume and pore size in carbon materials due to the presence of metal oxides, being the carbonaceous material responsible for the generation of microporous. In this study, it is observed the same trend, a predominance in microporosity is observed for the materials without the pre-oxidation step, which is related to the lower carbon loss.

In order to gain more information about the properties of the synthesized materials, metal and carbon content were analyzed after the different treatments (Table 2). Metal content does not suffer significant changes, with an average value of ca. 30 wt% and being Fe the predominant metallic species (practically 50% of the total metal content in all the cases). In contrast, the carbon content decreases gradually with the loading of KOH, this reduction more accentuated for the ACT-P set of materials (with the pre-oxidation step). In parallel, the oxygen concentration clearly increases, which indicates oxidation processes which achieve oxygenated carbon compounds and their metal oxides. On the other hand, the content of N, S and H gradually decreases compared to the initial oily sludge and is negligible for the most severe treatment conditions, probably due to its chemical oxidation during the synthesis procedure into gases, such as SO_x or NO_x (Shan et al., 2018; Wabo and Klepel, 2021).

Thus, summarizing the analysis of both sets of materials synthesized, the thermochemical activation applied promotes the formation of porous materials with meso- and micropores and higher surface area. As well as a composition with a high concentration of C and Fe content, which leads to its catalytic applications.

Boehm titration analyses were carried out to determine the solid samples surface functionality. Fig. S2 (available in supplementary material) shows the concentration of basic centers in mmol per gram of carbon with the KOH:solid mass ratio for both sets of materials. It could not accurately measure the acidic centers' concentration due to the interferences of organic and inorganic species, like silica or phenols, typically contained in biochar and similar materials (Tsechansky and Graber, 2014). The results indicate that all materials have basic organic moieties on their surface being this value enhanced with the KOH loading and is generally higher for the pre-oxidized samples. Other authors reported the predominance of basic groups (1.45–1.7 meq/g) after the thermochemical activation of sewage sludge, which also favours its catalytic application in the CWAO process (Marques et al., 2011).

The structural features of these materials have also been studied using XRD (Fig. 1 (a) and (b)). A very complex mixture of metal oxides and amorphous carbon is observed in the raw solid phase, where it is possible to distinguish peaks associated with the diffraction of SiO_2 ($\approx 21°$) or $CaCO_3$ ($\approx 29°$) (Ghayeb Zamharir et al., 2018; Wan et al., 2022). However, when KOH is used, significant changes are observed in the structure, being more significant in the absence of the pre-oxidation step. Regarding the materials synthesized with the pre-oxidation step, when KOH was used, the peaks associated with SiO_2 ($\approx 21°$) are not showed, emerging characteristics peaks of Fe: 44.3°, 64.1°, and 82.1° associated with the (220), (321) and (332) planes of this metal (Wen

Table 1

Textural properties of the synthesized materials with pre-oxidation step, and without pre-oxidation step using the solid phase from oily sludge.

	S_{BET} (m^2/g)	V_T (cm^3/g)	$V\mu$ (cm^3/g)	V_m (cm^3/g)
Pre-oxidized materials				
ACT-P 0.1	40 ± 11	0.095	0.024	0.071
ACT-P 1.1	276 ± 73	0.25	0.19	0.066
ACT-P 2.1	358 ± 1	0.38	0.13	0.25
ACT-P 3.1	519 ± 70	0.49	0.17	0.320
Non-oxidized materials				
ACT-NP 0.1	55 ± 6	0.11	0.027	0.082
ACT-NP 1.1	637 ± 4	0.50	0.11	0.39
ACT-NP 2.1	762 ± 43	0.61	0.15	0.46
ACT-NP 3.1	708 ± 56	0.59	0.37	0.22

Table 2

Metal content and elemental analysis for the carbonaceous materials synthetized with and without a pre-oxidation step for the different KOH:solid mass ratios.

	Total metals (%)	Fe (%)	C (%)	N (%)	H (%)	S (%)	O (%)
Oily sludge	34.1 ± 0.3	15.0 ± 0.1	45 ± 2	1.3 ± 0.1	4.5 ± 0.2	5.0 ± 0.2	10.1
Pre-oxidized materials							
ACT-P 0.1	39.6 ± 0.3	15.8 ± 0.1	38 ± 3	0.4 ± 0.1	0.40 ± 0.06	5.7 ± 0.4	15.8
ACT-P 1.1	34.6 ± 0.3	18.3 ± 0.1	28 ± 1	0.2 ± 0.1	1.2 ± 0.1	1.5 ± 0.3	34.8
ACT-P 2.1	34.6 ± 0.3	17.3 ± 0.1	22 ± 1	0.10 ± 0.01	1.3 ± 0.1	2.0 ± 0.2	40.0
ACT-P 3.1	37.5 ± 0.3	16.3 ± 0.1	20 ± 1	0.04 ± 0.02	1.3 ± 0.1	0.90 ± 0.03	40.3
Non-oxidized materials							
ACT-NP 0.1	38.7 ± 0.3	17.1 ± 0.1	40 ± 3	0.5 ± 0.1	0.20 ± 0.03	7.30 ± 0.04	13.3
ACT-NP 1.1	30.5 ± 0.2	18.8 ± 0.1	30 ± 1	–	1.2 ± 0.1	0.6 ± 0.1	37.7
ACT-NP 2.1	37.5 ± 0.3	18.5 ± 0.1	28 ± 3	–	1.1 ± 0.1	1.5 ± 0.2	32.2
ACT-NP 3.1	29.8 ± 0.2	15.6 ± 0.1	24 ± 1	–	0.9 ± 0.04	1.2 ± 0.1	37.5

et al., 2012) and other Fe species (such as Fe_3C and Fe_3O_4) (Jaiswal et al., 2021; Wu et al., 2011). It is important to note that some Fe species, such as Fe_3O_4, only appear on the pre-oxidized materials. The peaks at $\approx 26°$ and $\approx 43°$, corresponding to C (002) and C (101) lattice planes, respectively (Jiaofei Wang et al., 2017), indicate the existence of amorphous structures in the prepared carbon materials (Fan et al., 2022). It is important to note the materials synthesized with KOH showed a carbon peak slightly displaced at $\approx 29°$, which was also reported by other authors, which indicated its relationship with amorphous carbon (Li et al., 2020).

Finally, SEM analyses were carried out to investigate the surface morphology of the carbonaceous materials and settle (by carrying out SEM-EDX) its composition (see more details in supporting information). As shown in Fig. S3 (available in supplementary material), the microstructure of the initial solid phase sample is undefined and without any porosity. However, when KOH is used in the synthesis, the surface of the solids turns rough with slight traces of activation, as mentioned by previous authors who reported the KOH effect to create large pores and cavities (Jang et al., 2018; Ma et al., 2022). Compared to the raw sample, ACT-P displayed pores of different sizes and a more homogeneous surface (Fig. S4, available in supplementary material). A similar tendency is observed for samples without the pre-oxidation step (Fig. S5, available in supplementary material), with an increase in the porosity of the materials when using KOH in the synthesis. Moreover, when the ratio of KOH is increased and, therefore, the surface area, the sample's pore structure becomes more abundant, which evidences the porosity created. According to EDX microanalysis, Fe, C and O dominate on the surface, as elemental analysis and XRF previously determined.

3.2. Catalytic wet air oxidation experiments

In CWAO processes, the role of basic sites of the carbon surface has been considered beneficial for enhancing organic removal (Rocha et al., 2020). Additionally, metallic species and high porosity are key parameters to promote CWAO processes (Marques et al., 2011). Hence, for these catalytic assays, we have chosen 0:1 and 1:1 KOH mass ratio carbonaceous materials synthesized in the presence and absence of the pre-oxidation step (ACT-P 0.1: ACT-P 1.1; ACT-NP 0.1; and ACT-NP 1.1) which are those showing more significant differences in terms of surface basic sites concentration as well as textural and morphological properties, being Fe predominant on the surface (confirmed in the SEM images).

Fig. 2 a) shows the catalytic results in terms of soluble COD conversion with the reaction time for the different materials under study. Catalytic results show that the materials activated with KOH (ACT-P 1:1 and ACT-NP 1:1) promote a fast degradation of organic compounds, reaching COD removals by over 50–60 %, which might be attributed to enhancing their textural properties. Several authors have reported this influence, indicating a higher efficiency in CWAO processes using carbon materials with higher surface area (González et al., 2023; Rocha et al., 2020). Being the non-preoxidated material (ACT-NP 1.1), it

exhibits the best catalytic performance in terms of COD removal.

ACT-P 1.1 and ACT-NP 1.1 materials show similar Fe content (Table 2), and basic sites surface concentration (Fig. S3, available in supplementary material) but with different specific surface areas (276 m^2/g vs 637 m^2/g) and total pore volume (0.25 cm^3/g vs 0.50 cm^3/g). Hence, the catalytic data indicate that textural properties play a crucial role in the catalytic performance of the synthesized materials in the CWAO process, and the pre-oxidation step does not favour a better performance of the materials during the CWAO process.

Also, as mentioned above, the Fe content is a crucial player of the catalytic behaviour of these materials for its application in CWAO. Thus, to elucidate the role of the metallic species in the CWAO process, an additional catalytic run was performed over a metal-free activated sample. The solid phase of the oily sludge was firstly washed with HCl 2 M at 25 °C for 24 h in order to remove all the metallic species and then washed with milli-Q water until pH ≈ 7 and dried at 100 °C until no weight loss was detected (Feng et al., 2021). The resultant solid was thermally treated as described in the experimental section with a KOH mass ratio of 1:1 and without a pre-oxidation step (see details of characterization in supporting information, Table S2). This material was assessed in the CWAO of the spent-caustic wastewater under the same conditions as those of the other samples. Catalytic results after 2 h of reaction yielded a COD removal of 35 %, which is significantly lower than that of the metal-containing sample (ACT-NP 1.1) ca. 47 % despite this free-metal sample having a higher specific surface area (957 m^2/g). Therefore, these catalytic results confirm the paramount role of metallic species in the overall catalytic performance observed in the CWAO process.

Moreover, to confirm the catalytic activity of these carbonaceous materials, a WAO treatment was carried out in the absence of a catalyst, as well as using the raw solid particles from oily sludge as catalyst (CWAO 0) under the same reaction conditions used for the synthesized samples (Fig. 2 b)). In both cases, the degradation rates are significantly slower than that obtained using the material ACT-NP 1:1 as the catalyst. The CWAO 0 reaction shows the worst catalytic performance with ca. 30 %. of COD removal after 4 h. This result is even lower than the WAO treatment (ca. 40%), which might be attributed to this material's poor porosity and the partial solubilization of carbon species within the aqueous solution, which would increase aqueous organic loading. These two experiments confirm the outstanding activity of the synthesized materials for the treatment of refinery wastewater effluent and evidence the need to apply a thermochemical treatment to the raw solid particles.

Likewise, the catalytic performance of a metal-free commercial activated carbon with a high specific surface area (ca. 1000 m^2/g; CWAO NORIT) is also shown in Fig. 2 b). This material shows a COD degradation of ca. 50 % after 4 h of reaction, which is slightly lower than that obtained for the thermochemical treated sample (ACT-NP 1:1) but with significant differences in the initial degradation rate. This latter data would be a strong indication that although porosity is important, the presence of a high loading of metallic species plays a crucial role in the catalytic performance of the materials prepared in this work.
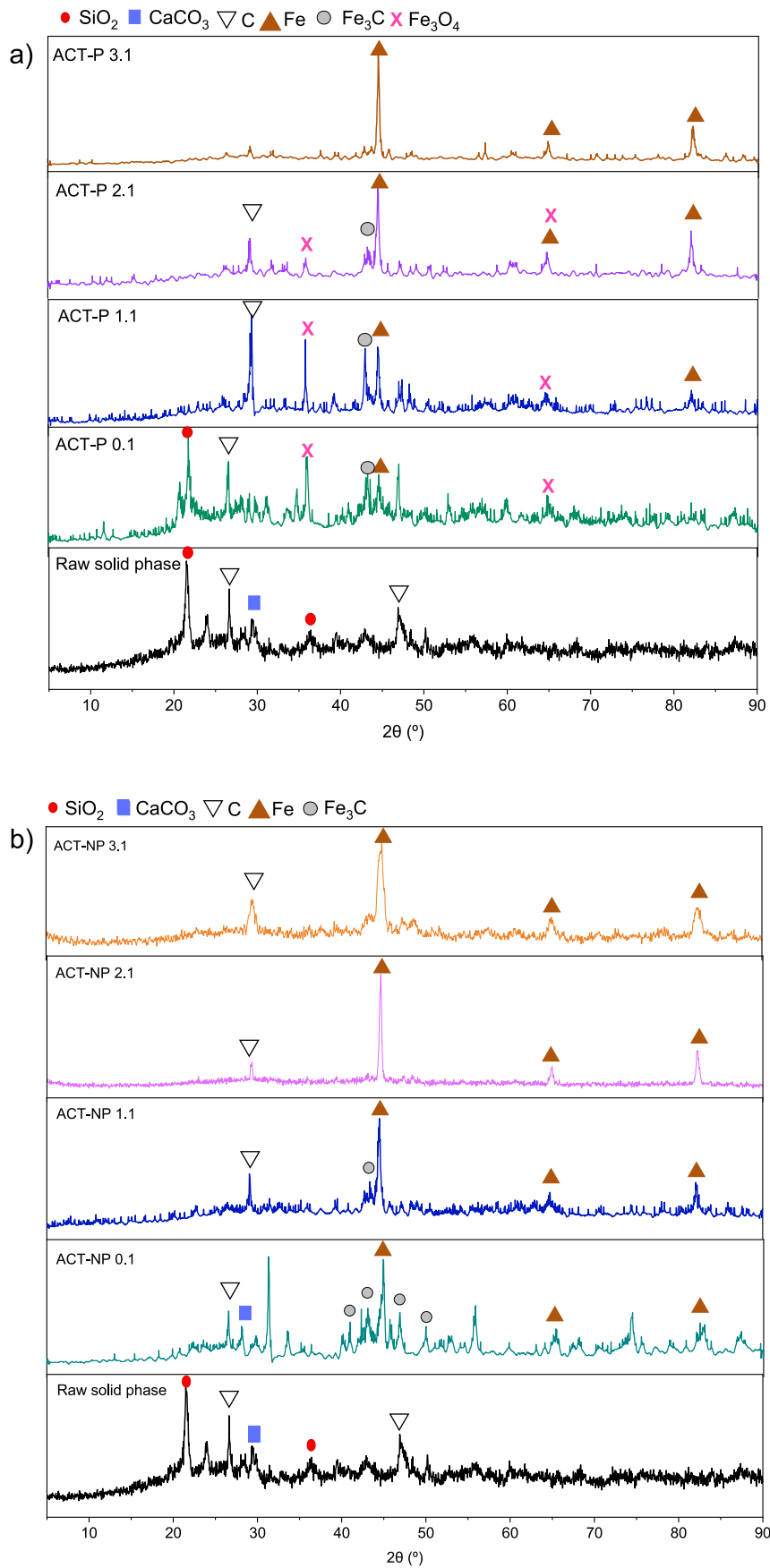
Fig. 1. XRD analysis for the synthetized materials by different KOH:solid mass ratios (a) with pre-oxidation step and (b) without pre-oxidation step.
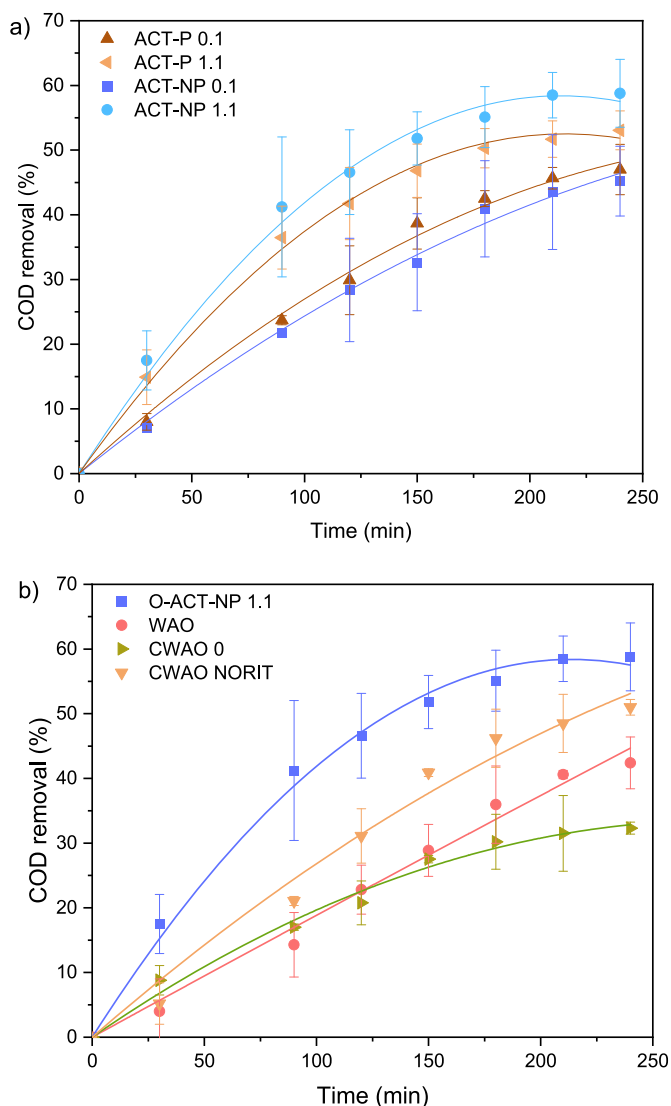
Fig. 2. a) COD removal in the CWAO reactions over the synthetized carbonaceous materials; **b)** Blank catalytic runs. Thermal WAO in the absence of catalyst (WAO); CWAO over the untreated oily sludge (CWAO 0); and CWAO over a metal-free commercial activated carbon (CWAO NORIT). The catalytic performance of the ACT-NP 1.1 sample is included in terms of comparison.

The basic sites of the solids also seem to play a crucial role in the degradation of this pollutant. When basicity decreased, as for the solid washed with HCl, c.a 0.0075 mmol base/g C or the carbon NORIT 0.0012 mmol base/g C, COD degradation decreased as well, finding a higher degradation with the increased basic sites.

Other authors have also reported the effect of catalytically active metals (especially Fe) and surface functional groups. The Fe content and the presence of basic sites on the surface of the materials promote a higher CWAO activity (Marques et al., 2011). The Fe content (black squares in Fig. 3) in the catalyst could promote the $^{\bullet}OH$ radicals generation during the CWAO process (Archila et al., 2020). González et al., reported the important role of these basic sites (red circles in Fig. 3) during the oxidative CWAO process to degrade the pollutants present in the refinery wastewater properly. The basic groups can react with the C–N bonds present in the spent caustic refinery wastewater and oxidize it to other intermediates (acetic acid, ammonium, etc.) (González et al., 2023). Therefore, as shown in Fig. 3, the combination of both Fe content and basic sites are essential for the better CWAO performance of these new carbonaceous materials in comparison with commercial activated carbons (NORIT) and metal-free carbons.
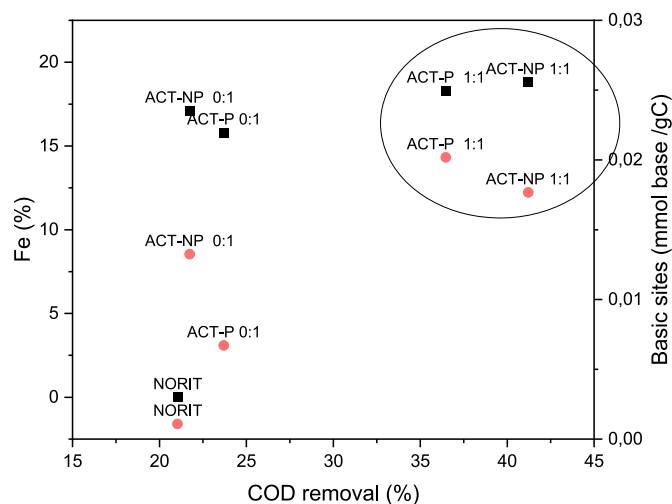

Fig. 3. Comparison of the effect of Fe content and basic sites of the materials, in terms of COD removal, after 90 min of CWAO reaction. Fe is represented with squares (■) and basic sites with circles (●).

To further understand the chemical surface composition of these materials, XPS analysis were carried out. As shown in Fig. 4, the C1s spectra of the materials were decomposed into four peaks after deconvolution, located at $\approx$284, 286, 287 and 289 eV which correspond to C–C/C–H, C–O, C═O and O–C═O functional band, respectively (Pereira Lopes and Astruc, 2021; Sheng et al., 2011). The functional bands C–O and C═O exhibit a higher value for the materials ACT-P 1.1 and ACT-NP 1.1. The C–O functional band shows a clear correlation with the catalytic activity of these materials, which increases as the C–O groups on the surface of the materials become more abundant (Fig. S6). The material ACT-NP 1.1 showed the higher C–O group in its surface (34,75%), and the higher catalytic activity regarding COD removal. Previous authors reported the same effect, which indicated the agreement of the CWAO activity of carbon materials with the content of carboxylic and carbonyl groups on their surface (Marques et al., 2011; Wang et al., 2014).

Furthermore, Fe2p spectra were studied, to assess iron presence on the surface of the materials. The signals at $\approx$712 and 725 eV can be assigned to Fe^{3+} (Chu et al., 2018), which is the principal iron species in all the materials. Also, Fe^{2+} species were detected at $\approx$710 and 724 eV (Chu et al., 2018), but with lower content (Fig. S7, available in supplementary material). However, non-significant differences were found for the analyzed materials.

Another key factor in settling the stability and commercial suitability of the tested catalysts is the leaching of metals during the reaction and, its reusability in successive catalytic cycles. ACT-P 1.1 and ACT-NP 1.1 samples were chosen for this study under the preceding reaction conditions. The catalytic performance of both materials was compared in three successive catalytic cycles (Fig. 5). The leaching of metals was determined by the ICP-AES analysis of the liquid phase after the reaction. The initial concentration of metals in the industrial wastewater was K (195 mg/L) and Si (29 mg/L), followed by other metals like Ca or Al, with 8 and 5 mg/L, respectively. After the three consecutive CWAO cycles, the metal content of the wastewater was kept constant for both catalysts, which indicates, no significant leaching of any metal, determined by ICP analysis. In particular, Fe content in the refinery wastewater presents the same concentration before and after the CWAO reactions, with 1 g/L. Furthermore, XRF analysis performed in the spent catalysts gave a metal content in the same range as the fresh one ($\approx$18% for both catalysts). These data confirm the high stability of the metal species under the tested reaction conditions of the synthesized materials and discard the contribution of homogenous catalysis.

On the other hand, results in Fig. 5 show that after the three catalytic cycles, both catalysts evidence close COD removal (with a decrease of
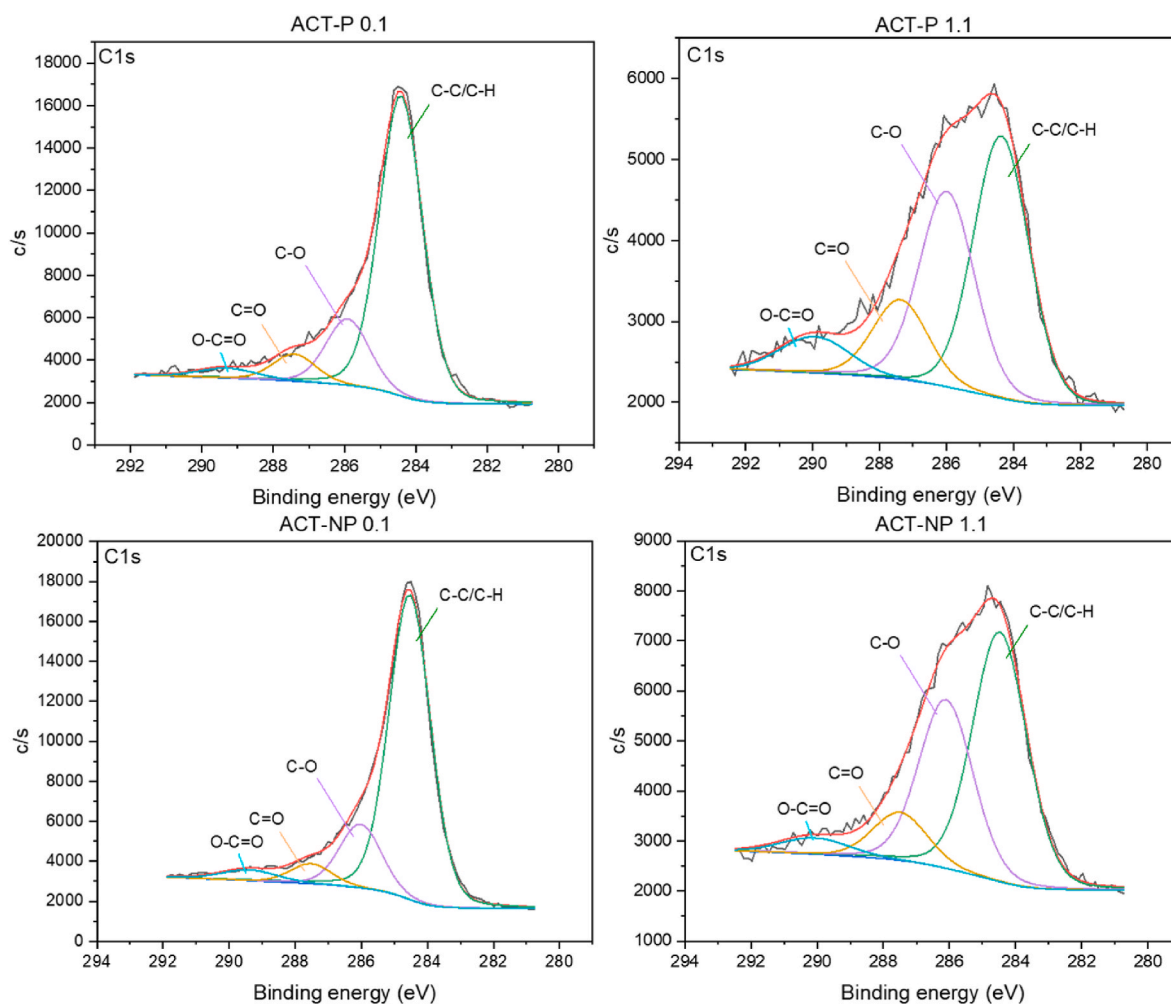
Fig. 4. C1s spectra of ACT-P 0.1, ACT-NP 0.1, ACT-P 1.1 and ACT-NP 1.1.

only 5%) values after 4 h of a reaction than that obtained for the fresh ones. Nevertheless, the degradation rate gradually decreases in the successive catalytic cycles for the pre-oxidized sample (ACT-P 1.1; Fig. 5 a. and Table S3, available in supplementary material). In contrast, this trend is not observed for the unoxidized sample which keeps a similar catalytic performance in terms of COD removal rate after the three catalytic cycles. Hence, better stability of the un-oxidized sample (ACT-NP 1.1; Fig. 5 b) might be preliminary inferred from these catalytic results.

This partial in-situ deactivation of the catalyst cannot be attributed to the loss of metallic species as leaching within the liquid phase was negligible and significant deposition of organic deposits has also been ruled out in TGA analysis (data not showed). Hence, to elucidate other possible causes for the decay of the catalytic activity XRD analyses of the samples after each catalytic cycle were conducted (Fig. S8, available in supplementary material). Some changes are detected for the pre-oxidized sample which would correlate with its lower stability in successive reactions. The peaks associated with Fe_3O_4 disappear in the first cycle, which may be attributed to its interaction with O_2 during the CWAO reactions, promoting its transformation into Fe_2O_3, as evidenced in the XRD diffractogram with a diffraction peak at $\approx 33°$ (Archila et al., 2020; Das et al., 2020). This fact affects mainly the reaction rate, which decreased progressively for the pre-oxidized material (Table S3, available in supplementary material). In contrast, the unoxidized sample retains the same structure as the fresh catalyst and thus exhibits similar catalytic performance.

The fast biodegradability of the treated effluents obtained after the

CWAO process was performed by means of respirometric tests with an activated sludge culture acclimatized for months to a biodegradable substrate such as sodium acetate (Fig. 6). The untreated refinery wastewater showed an initial biodegradability of 31 %. After the WAO and CWAO 0 treatments, the biodegradability increased slightly, however, they are not efficient treatments to achieve a biodegradable effluent.

Nevertheless, after the oxidation over the ACT-P 1.1 and ACT-NP 1.1 catalysts, these values increased to 77 % and 84 %, respectively. These results clearly evidence that the carbonaceous materials synthetized can catalyze the degradation of refractory and non-biodegradable organic pollutants initially present in this refinery wastewater towards less complex and more biodegradable molecules hence allowing its potential treatment in the conventional biological process of wastewater treatment plant of the refinery. Thus, the study strategy allows the creation of a circular process in the refinery plant, achieving the 2050 objectives of zero waste and waste valorization (Fuels Europe, 2018).

To further understand the degradation of compounds during the CWAO treatment of this spent caustic refinery wastewater, a previous work of this group determined the degradation mechanism (González et al., 2023). The potential oxidation reactions are based on the compounds identified in the spent caustic refinery wastewater, mainly MDEA (methyldiethanolamine). After these oxidative reactions, several by-products are generated (ammonium, acetic acid, or CO_2, among others), which are directly correlated with the biodegradability results (For more information, look up González et al., 2023).
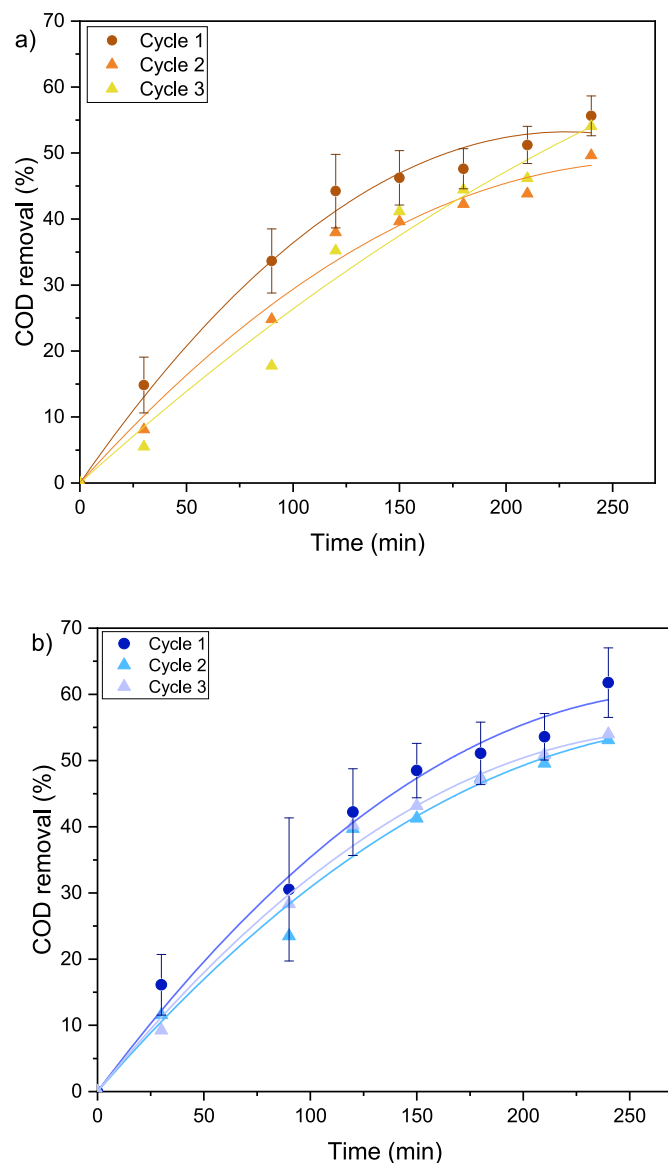
Fig. 6. Biodegradability of treated wastewater after different CWAO reactions.

Fig. 5. Reusability for the carbonaceous synthetized material in three catalytic cycles a) ACT-P 1.1 and b) ACT-NP 1.1.

3.3. Comparison with similar processes

Catalytic wet air oxidation treatment has been widely studied for the treatment of industrial wastewater. For this purpose, different catalysts have been tested, such as noble metals and rare earth oxide or metal-free carbon materials as an alternative to these (Wang et al., 2007; Rocha et al., 2020). The potential of carbon materials based on waste feedstock has increased its interest due to their improved textural and chemical properties, using thermal and chemical treatments (Rocha et al., 2020). These waste-carbonaceous materials have demonstrated their effectiveness as catalysts for the CWAO process while also exhibiting a reduced environmental footprint, thanks to the utilization of a residue as a precursor (Marques et al., 2011; Quintanilla et al., 2010; Santiago et al., 2005). Some works have focused on the valorization of refinery oily sludge for the synthesis of new carbon materials as adsorbents or supercapacitors (Andrade et al., 2009; Fan et al., 2022; Li et al., 2017; Liu et al., 2022; Mohammadi and Mirghaffari, 2015; Jun Wang et al., 2017). However, to the best of our knowledge, their application as a catalyst in the CWAO process has not been reported yet.

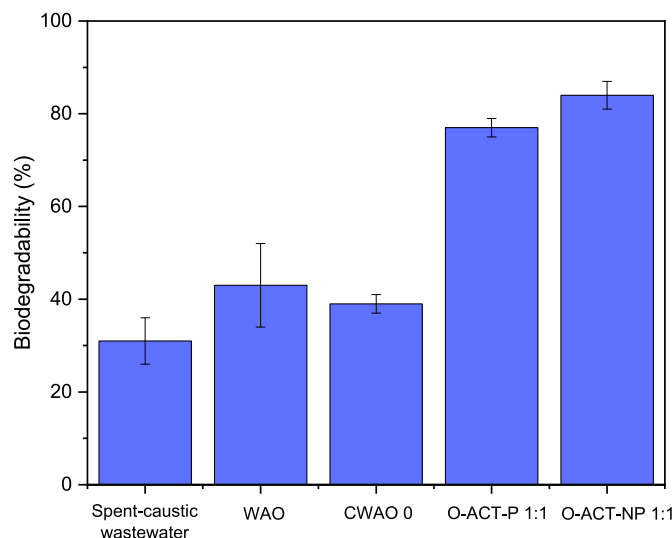Furthermore, the novelty of this work lies in the use of new carbonaceous materials from oily sludge for CWAO application to treat a real refinery spent caustic wastewater (Barge and Vaidya, 2018, 2020), instead of using model compounds as most of the works found in the literature.

Table 3 summarizes the most significative studies, based on a high COD removal or the use of a waste as catalyst precursor, always focused on the CWAO treatment of a spent caustic effluent. The bulk of these studies use noble metals or single/mixed oxides as catalysts, with significant COD removal but at a high cost (Barge and Vaidya, 2018; Rocha et al., 2020) or without demonstrate the recyclability of these catalysts (Barge and Vaidya, 2020; Chen and Cheng, 2013). Chen et al. reported up to 95% of COD degradation, as well as, phenol and petroleum oxidation using MnO_x-CeO_x/γ-Al_2O_3 catalyst (Chen and Cheng, 2013). Also, Barge et al. achieved a 94% of COD removal using $FeSO_4$ as catalyst for the treatment of a model compound, such as sodium sulfide (Barge and Vaidya, 2020). However, the use of noble or toxic metals is related to environmental problems as the deactivation phenomena are common, particularly the leaching of the metal phases to the liquid medium (Rocha et al., 2020). The use of other catalysts, such as activated carbons or metal-free carbons, for the treatment of spent caustic effluents, as well as waste-based carbons has not been studied. The works of this group have studied this possibility until the present day (González et al., 2023).

González et al. reported the use of petcoke as catalyst for CWAO treatment of spent caustic refinery wastewater, reaching 30% of COD removal at mild conditions, similar at those reported of other authors (González et al., 2023). The present work proposes a new catalyst for this CWAO treatment, using the solid phase of oily sludge. The COD removal up to 60%, together with the high stability and recyclability of these materials and a significant increase of the effluent biodegradability (80%), makes the use of these catalysts environmentally friendly and thus aligns with the European objectives for 2030. The results of this study offer a novel strategy for the treatment of this refinery effluent and, at the same time, the valorization of oily refinery sludge into new materials.

This work proposes the catalytic application of oily-sludge solid particles and introduces a circular process for refineries, enabling the reintegration of these new materials into the refinery system for the treatment of actual wastewater. This novel strategy not only valorizes and treats refinery wastes, reducing their environmental impact, but also establishes a Circular Economy approach. This aligns with the EU's 2050 objectives for sustainable refinery practices. To further improve the implementation of this process, different synthesis methodologies could be studied, adding different metallic species active in catalysis. In

Table 3
Summary of studies on CWAO of refinery spent caustic wastewater.

Catalyst	Feedstock	Spent caustic effluent	Reaction conditions	COD removal	Reference
Noble catalyst	Ru/GO	Model compounds	190 °C; 20 bar of O2; 0.02 g/L catalyst	75%	Barge and Vaidya (2018)
	MnO_x-CeO_x/γ-Al_2O_3	Real spent caustic wastewater	200 °C; 20 bar of air; 1 g/L catalyst	95%	Chen and Cheng (2013)
Metal oxides	$FeSO_4$	Model compounds	100 °C; 7 bar of O_2; 0.8 g/L catalyst	94%	Barge and Vaidya (2020)
	IVKAZ	Real spent caustic wastewater	50 °C; 8 bar of air; 0,1 g/L catalyst	42%	Elmi et al. (2021)
Waste-based carbons	Petcoke	Real spent caustic wastewater	200 °C; 50 bar of air; 1 g/L catalyst	30%	González et al. (2023)
	Solid phase of oily sludge	Real spent caustic wastewater	200 °C; 50 bar of air; 1 g/L catalyst	60%	This work

addition, a techno-economical assessment must be carried out to determine the costs of the proposed technology, compared with the current management.

4. Conclusions

New carbonaceous materials have been synthesized and employing the solid particles derived from a refinery oily sludge as feedstock through thermochemical activation using KOH as and activating agent. The synthesized materials evidence the development of meso and microporosity, along with high specific surface area (up to 762 m^2/g). Their application as catalysts in CWAO of a non-biodegradable spent caustic refinery wastewater has shown good performance in terms of COD removal (up to 60% for the best-performing material ACT-NP 1.1). The Fe content (ca. 18%) and the basic sites on its surface (ca. 0.018 mmol base/g C) are essential parameters for its catalytic application in CWAO reaction. Also, the optimum material (ACT-NP 1.1) displays good reusability in three consecutive catalytic cycles without leaching of metallic species. Moreover, the treated refinery wastewater exhibits a notably higher biodegradability (up to 84%), which allows its treatment in conventional biological processes. The conducted studies have clearly demonstrated the feasibility of recycling solid particles from highly contaminated waste and their subsequent use as valuable catalytic materials. These findings pave the way for a novel circular strategy aimed at the valorization and treatment of both the solid phase and spent caustic refinery wastewater generated within the same refinery. This approach not only facilitates the synthesis of new waste-based catalysts but also promotes the production of a biodegradable aqueous effluent. Consequently, this strategy holds significant potential for reducing environmental impact while aligning with the principles of a Circular Economy. This new proposal, shown in this work, aligns with the new vision for 2050 refineries, where is required circularity, zero waste and enhanced sustainability bullet points achieved in this work. Moreover, for the implementation of this technology, a techno-economical assessment is needed to determine the energetic and operative costs and demonstrate its feasibility compared to current technology, carried out for the treatment of both wastes, the sludge, and the wastewater.

CRediT authorship contribution statement

Sara Jerez: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **María Ventura:** Writing – original draft, Supervision, Investigation, Data curation, Conceptualization. **Fernando Martínez:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization. **María Isabel Pariente:** Writing – original draft, Validation, Methodology, Investigation, Data curation. **Juan Antonio Melero:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Juan Antonio Melero Hernandez reports financial support was provided by Spanish Ministry of Science, Innovation and Universities.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2024.121606.

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