

Article

Pt/MnO_x/C Catalysts from Electrolytic Manganese Residue and Oil Sludge for VUV Photocatalytic CO Oxidation: Synergistic Bio-Pretreatment and Polyphenol-Mediated Pt Dispersion

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Abstract

The valorization of hazardous industrial wastes into high-performance catalytic materials presents a compelling route to address both environmental pollution and resource scarcity. This work presents a closed-loop strategy for the fabrication of Pt/MnO_x/C composite catalysts using electrolytic manganese residue and oil sludge. The strategy integrates anaerobic co-fermentation with mixed halophilic desulfurizing bacteria and polyphenol-mediated Pt dispersion via blueberry extract. The optimal catalyst achieves an exceptional vacuum ultraviolet photocatalytic carbon monoxide oxidation efficiency of 97.79% at ambient temperature, with an endpoint-derived apparent pseudo-first-order rate constant of 0.128 min^{−1}, outperforming a commercial Pt/Al₂O₃ reference (2.5 wt% Pt) by a factor of 4.4 in apparent rate constant (equivalent to 1.7-fold in 30 min conversion efficiency) while utilizing less than half the noble metal loading (1.12 wt% Pt). Comprehensive characterization reveals a genuine structural synergy arising from (i) ultrafine Pt⁰ nanoparticles (2.1 nm) anchored at MnO_x–carbon interfaces, (ii) a mixed-valence MnO_x matrix (Mn²⁺/Mn³⁺ = 1.8:1) with abundant surface oxygen defects (28.3% of the O 1s envelope, an upper bound corroborated by EPR spectroscopy) for reactive oxygen species trapping, and (iii) Nitrogen-doped carbon domains (2.8 atomic percent) that facilitate electron transfer. In situ diffuse reflectance infrared Fourier-transform spectroscopy and kinetic analyses are consistent with a Langmuir–Hinshelwood-type mechanism, where CO is activated on Pt⁰ and reacts with O₂ dissociated at oxygen vacancies under vacuum ultraviolet excitation. This work establishes a sustainable paradigm for transforming industrial wastes into high-value photocatalysts, offering a viable pathway toward low-temperature air purification and circular resource utilization.

Keywords: Pt/MnO_x/C catalyst; vacuum ultraviolet photocatalysis; CO oxidation; electrolytic manganese residue; oil sludge; anaerobic co-fermentation; polyphenol-mediated synthesis



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1. Introduction

Carbon monoxide (CO) represents one of the most pervasive atmospheric pollutants arising from incomplete combustion of carbonaceous fuels in industrial processes, vehicular emissions, and residential heating [1]. With global anthropogenic CO emissions exceeding 500 million tonnes annually, this colorless, odorless gas poses severe threats to human health through the formation of carboxyhemoglobin, which impairs oxygen transport in

blood, and contributes to the photochemical generation of ground-level ozone and secondary organic aerosols [2]. Conventional CO abatement strategies rely predominantly on thermal catalytic oxidation, which necessitates elevated operating temperatures (typically 150–400 °C) to achieve satisfactory conversion efficiencies. While noble metal catalysts based on platinum (Pt) and palladium (Pd) exhibit exceptional low-temperature activity [3], their industrial deployment is severely constrained by prohibitive costs, susceptibility to poisoning by sulfur and chlorine species, and the substantial energy penalty associated with maintaining high reaction temperatures. Non-noble metal alternatives, particularly manganese oxides (MnO_2 , Mn_3O_4), demonstrate promising intrinsic activity at ambient conditions but suffer from poor thermal stability, rapid deactivation via sintering, and insufficient resistance to moisture and competing pollutants [4]. These limitations collectively underscore an urgent imperative to develop innovative catalytic systems capable of achieving efficient CO oxidation under mild conditions while circumventing the dependency on scarce noble metal resources.

Vacuum ultraviolet (VUV) photocatalysis has emerged as a transformative paradigm for low-temperature pollutant degradation, leveraging the extraordinary photon energy of sub-200 nm radiation to directly activate both catalyst surfaces and gas-phase molecules. The 185 nm emission line from low-pressure mercury lamps, with a photon energy of 6.7 eV, exceeds the dissociation thresholds of molecular oxygen and water vapor, thereby generating a rich inventory of reactive oxygen species (ROS) including atomic oxygen, hydroxyl radicals, and ozone without requiring thermal activation [5–7]. Unlike conventional ultraviolet (UV, $\lambda > 200$ nm) photocatalysis, which depends critically on the bandgap energetics of semiconductor photocatalysts, VUV-driven processes operate through a dual mechanism: direct photolysis of gas-phase species and photoexcitation of surface-active sites, enabling catalytic oxidation even on nominally wide-bandgap materials. Recent studies have demonstrated that Pt nanoparticles supported on reducible metal oxides such as CeO_2 and MnO_x exhibit synergistic VUV photocatalytic activity, wherein Pt facilitates CO adsorption and activation via back-donation from filled Pt 5d states to the CO $2\pi^*$ antibonding orbital, while oxygen vacancies in the oxide support serve as trapping and dissociation sites for photogenerated oxygen species [3–5]. However, the practical implementation of such catalysts remains hindered by the high noble metal loadings required to achieve meaningful activity, the energy-intensive synthesis protocols involving organic solvents and high-temperature calcination, and the environmental footprint associated with virgin metal precursors and synthetic supports.

The valorization of industrial solid wastes into functional materials represents a compelling strategy to address simultaneously the challenges of resource scarcity and environmental contamination. EMR, the predominant solid byproduct of electrolytic manganese metal production, is generated at a staggering rate exceeding 10 million tonnes annually in China alone. Characterized by complex mineralogy comprising 23.5 wt% SO_3 , 13.2 wt% SiO_2 , 15.2 wt% CaO , 13.1 wt% Fe_2O_3 , and 10.2 wt% MnO (Table S1 in the Supporting Information), EMR presents formidable disposal challenges due to its high sulfur content, heavy metal enrichment (Pb, Hg, Cr, Cd), and alkaline nature [8–11]. The inherent presence of manganese and iron oxides in EMR, coupled with its calcium-rich matrix, renders it an intriguing yet underexploited precursor for catalytic materials, provided that the deleterious sulfur and heavy metal components can be effectively stabilized within a robust matrix. Oil sludge, a hazardous byproduct of petroleum refining and storage operations, constitutes another pressing environmental concern, with global generation estimated at 60 million tonnes per year. This complex mixture typically contains 30–40 wt% extractable petroleum hydrocarbons (C_{10} – C_{50}), 20–30 wt% heavy oil fractions, 15–25 wt% inorganic residues, and 10–20 wt% water (Table S1), alongside significant concentrations

of toxic metals and persistent organic pollutants [12,13]. The carbonaceous nature of oil sludge, however, offers a unique opportunity: when thermally processed under controlled conditions, the organic fraction can be converted into a hierarchically porous carbon scaffold with tunable surface chemistry, while the inherent mineral content contributes to the formation of metal oxide phases. The critical challenge lies in achieving sufficient structural organization and surface functionality to support catalytically active species, rather than producing amorphous, low-surface-area char [14,15].

Biological pretreatment of complex organic matrices through anaerobic microbial fermentation offers an environmentally benign and energetically favorable approach to deconstruct recalcitrant hydrocarbons into smaller molecular building blocks. Mixed consortia of desulfurizing and halophilic bacteria have demonstrated remarkable capabilities in metabolizing petroleum-derived organics under anaerobic conditions, producing short-chain fatty acids, alcohols, and biogenic gases while simultaneously modulating the redox environment through sulfate reduction [16,17]. The extracellular polymeric substances (EPS) secreted during microbial growth can template the formation of hierarchical pore structures upon thermal processing, while the metabolic byproducts—particularly sulfide and organic acids—can induce in situ reduction and complexation of transition metal ions, creating precursors for catalytically active mixed-valence oxide phases. However, the direct carbonization of biologically pretreated waste matrices typically yields carbons with poorly controlled porosity and unoptimized surface chemistry, necessitating a secondary functionalization step to anchor and disperse catalytic active sites. Plant-derived polyphenols, abundant in agricultural and food processing wastes, have attracted considerable attention as sustainable alternatives to synthetic reducing agents and stabilizers in nanoparticle synthesis. The polyphenol backbone serves as a capping agent, preventing nanoparticle agglomeration through steric stabilization and metal–phenolate coordination [18,19]. Upon thermal treatment, polyphenols contribute to the carbonaceous scaffold, while co-extracted proteins and amino acids in the crude botanical extract provide nitrogen for the formation of nitrogen-doped carbon domains. These domains can enhance electrical conductivity and modulate the electronic structure of supported metal nanoparticles through metal–support interactions. The integration of biological pretreatment with polyphenol-mediated functionalization thus presents a compelling, fully biogenic pathway to engineer high-performance catalytic materials from waste streams.

Despite these individual advances, a systematic investigation into the synergistic coupling of industrial waste precursors (EMR and oil sludge), biological pretreatment (mixed halophilic desulfurizing bacteria), and polyphenol-mediated noble metal dispersion for VUV photocatalytic CO oxidation remains conspicuously absent from the literature. Specifically, the following critical knowledge gaps persist: (i) the optimal formulation and processing parameters for converting EMR–oil sludge mixtures into high-surface-area, hierarchically porous carbon–metal oxide composites; (ii) the mechanistic roles of bacterial fermentation in hydrocarbon decomposition, pore structure templating, and metal ion speciation; (iii) the capacity of plant polyphenols to mediate the in situ reduction, dispersion, and stabilization of ultrafine Pt nanoparticles on waste-derived supports; (iv) the nature and dynamics of active sites under VUV irradiation, including the interplay between Pt⁰, MnO_x oxygen vacancies, and N-doped carbon domains; and (v) the long-term catalytic stability and resistance to deactivation under realistic operating conditions. A closed-loop and sustainable strategy is proposed for the fabrication of Pt/MnO_x/C composite catalysts from EMR and oil sludge. This strategy integrates anaerobic co-fermentation with mixed halophilic desulfurizing bacteria, polyphenol-mediated Pt dispersion via blueberry extract, and controlled thermal processing (Figure 1). The systematic experiments and comprehensive structural characterization were designed, carried out and adopted to explore the

synergistic advantages and efficient oxidation mechanisms for CO. This work establishes a paradigm for transforming hazardous industrial wastes into high-value photocatalytic materials, offering a scientifically rigorous and technologically viable pathway toward sustainable air purification and circular resource utilization.

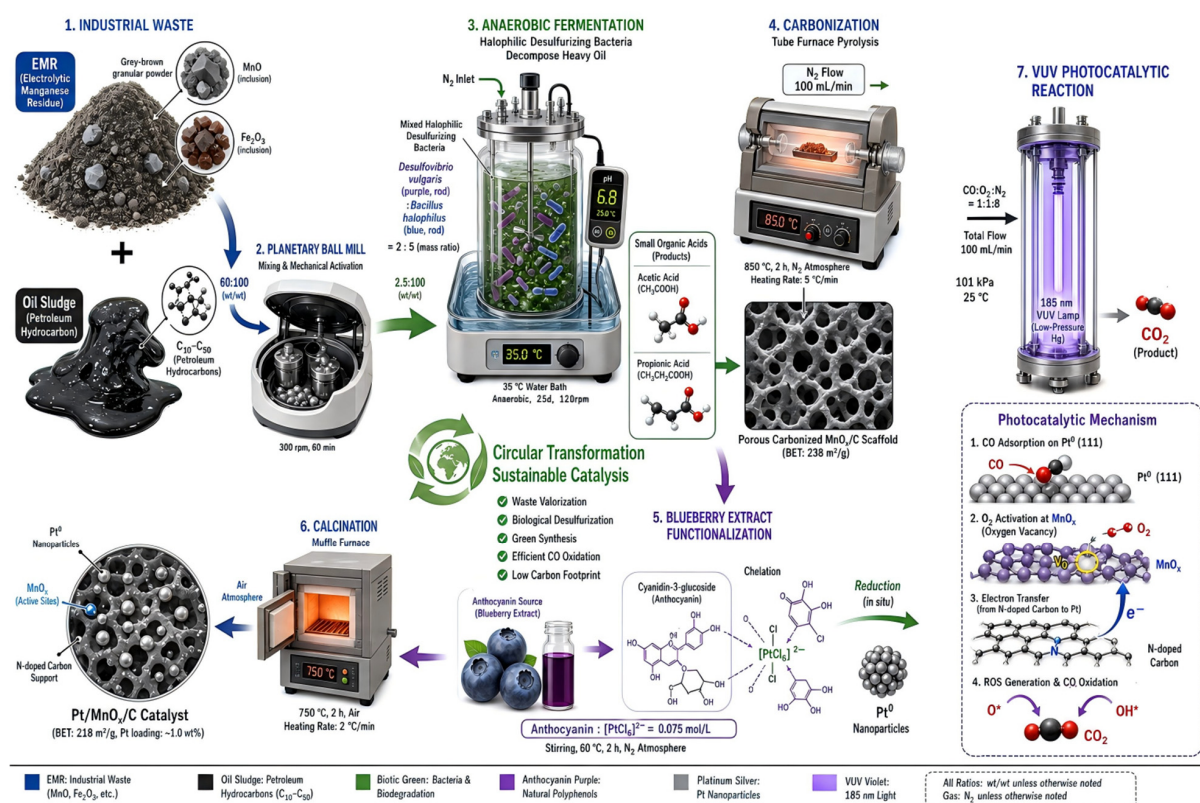


Figure 1. Schematic illustration of the sustainable fabrication and VUV photocatalytic mechanism (The Figure was generated with the assistance of artificial intelligence for drawing the graphics).

* The species adsorbed on the surface of the catalyst.

2. Materials and Methods

2.1. Materials

EMR was sourced from Guizhou Nengkuang Manganese Industry Group Co., Ltd. (Guizhou, Tongren, China), which was air-dried at 105 °C for 24 h, mechanically crushed, and sieved to a particle size of <74 µm (200 mesh) prior to use. Oil sludge was obtained from Shaanxi Yanchang Petroleum Refining & Chemical Co. (Yanan, China). The sludge was homogenized by mechanical stirring at 60 °C for 2 h to ensure representative sampling. The composition was determined by Soxhlet extraction with toluene (analytical grade, 99.9%, Sinopharm Chemical Reagent Co., Shanghai, China). Blueberry extract (*Vaccinium corymbosum*, ≥80% polyphenols) was supplied by Shanxi Chengzhi Biotechnology Co. (Xinzhou, China). The commercial blueberry extract was a crude botanical preparation containing co-extracted proteins and amino acids. The compositional analyses indicated a total protein content of 4.8 ± 0.3 wt%, a free amino acid content of 2.1 wt%, and a total nitrogen content of 0.77 wt% (Table S2). The principal free amino acids included asparagine, glutamine, and arginine. These nitrogen-containing constituents served as nitrogen sources during subsequent thermal treatment. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, ≥99.9%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The mixed halophilic desulfurizing bacteria consortium (strains listed in Table S5) was obtained from the China General Microbiological Culture Collection Center (CGMCC). All other reagents—sodium chloride

(NaCl, $\geq 99.5\%$), potassium dihydrogen phosphate (KH_2PO_4 , $\geq 99.0\%$), magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99.0\%$), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$), ammonium iron(II) sulfate hexahydrate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\geq 99.0\%$), sodium thioglycolate ($\text{C}_2\text{H}_5\text{NaO}_2\text{S}$, $\geq 98.0\%$), and sodium lactate solution ($\text{C}_3\text{H}_5\text{NaO}_3$, 60% *w/w*)—were of analytical grade and obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Deionized water (resistivity 18.2 M Ω cm) was prepared using a Milli-Q Direct 8 system (Millipore, Billerica, MA, USA). Nitrogen gas (N_2 , 99.999%) and certified CO/air gas mixtures (CO:air = 1:10,000 (*v/v*), $\pm 2\%$ uncertainty) were supplied by Linde Gas (Suzhou, China). Detailed material characterization for EMR, oil sludge, and blueberry is provided in Supporting Information (Tables S1 and S2).

2.2. Catalyst Preparation

The catalyst was synthesized via a five-step continuous protocol. Step I (mechanical activation): EMR and oil sludge were mixed at mass ratios of 12.5:100 to 75:100 and ball-milled at a ball-to-powder ratio of 20:1 and 300 rpm for 2 h using ethanol as a process control agent. The resulting composite was recovered by rotary evaporation at 60 °C, vacuum-dried at 80 °C for 12 h, and ground to pass a 100-mesh sieve. Step II (anaerobic co-fermentation): The Mn–oil sludge composite was inoculated with a mixed halophilic desulfurizing bacterial consortium (desulfurizing:halophilic = 1:5 to 3:5, 109 CFU mL^{−1}) at bacteria:substrate ratios of 0.25:100 to 3.25:100 (*w/w*) in anaerobic serum bottles. Fermentation proceeded at 20–50 °C and 120 rpm for 5–25 days; the natural buffering capacity of EMR maintained pH at 6.5–7.5. The specific conditions adopted in each screening stage are listed in the corresponding table captions; the final optimal conditions used for characterization and catalytic tests were 35 °C, 25 days, and 120 rpm. Fermentation was stopped after the prescribed duration, and TOC removal was determined at the end of each run. The fermented product (FP) was recovered by centrifugation, washed, and vacuum-dried at 80 °C for 24 h. Step III (carbonization): FP was carbonized in a tube furnace under N_2 flow (100 mL min^{−1}) at 550–850 °C for 2–6 h (heating rate 5 °C min^{−1}), yielding carbonized MnO_x/C material (CMO, 45–65 wt% yield) after grinding and sieving to <150 μm . Step IV (polyphenol-mediated Pt dispersion): CMO was dispersed in aqueous blueberry extract (0.1:100 to 4.5:100, *w/w*), ultrasonicated for 30 min, and magnetically stirred for 2 h. H_2PtCl_6 solution (0.005–0.075 mol L^{−1}, liquid-to-solid ratio 0.4–0.8 mL g^{−1}) was then added dropwise, and the mixture was vigorously stirred at 25 °C for 4 h to achieve in situ reduction of Pt(IV) to Pt(0) by polyphenol moieties, as monitored by UV-vis spectroscopy. The slurry was aged for 4–12 h, filtered, washed, and vacuum-dried at 80 °C for 12 h to obtain the Pt-impregnated precursor (Pt-CMO-P). Step V (controlled calcination): Pt-CMO-P was calcined in a muffle furnace under static air at 350–750 °C for 2–6 h using a slow heating rate of 2 °C min^{−1} to prevent Pt sintering, affording the final Pt/ MnO_x/C catalyst with an overall synthetic yield of 25–35 wt%. For the optimal catalyst, calcination was performed at 750 °C for 6 h in static air. The thermal behavior of the carbonized MnO_x/C material was investigated by thermogravimetric and differential scanning calorimetry analysis in static air (Figure S7), while post-calcination elemental analysis was used to assess the residual carbon content of the final catalyst. The catalyst selected for comparative testing and detailed characterization, hereafter referred to as the optimal catalyst, was prepared using an EMR:oil sludge mass ratio of 60:100, a bacteria:substrate mass ratio of 2.5:100, fermentation at 35 °C for 25 days, carbonization at 850 °C for 4 h, a blueberry extract:CMO mass ratio of 3.75:100, an H_2PtCl_6 concentration of 0.075 mol L^{−1} at a liquid-to-solid ratio of 0.8 mL g^{−1}, and calcination at 750 °C for 6 h in static air. Two control samples were prepared under otherwise identical optimal conditions: Control-1 (without desulfurizing bacteria, inoculated with halophilic bacteria only) and Control-2 (without blueberry extract,

with Pt loaded by H₂ reduction instead of polyphenol-mediated reduction). A commercial Pt/Al₂O₃ catalyst (2.5 wt% Pt) was employed as an industrial reference.

2.3. Characterization

The catalysts were characterized by X-ray diffraction (XRD, Rigaku SmartLab, Tokyo, Japan), N₂ adsorption–desorption (Micromeritics ASAP 2460, Micromeritics Instrument Corporation, Norcross, GA, USA), transmission electron microscopy (TEM/HRTEM/STEM, JEOL JEM-F200, JEOL Ltd., Tokyo, Japan), X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+, Thermo Fisher Scientific, Waltham, MA, USA), inductively coupled plasma–atomic emission spectrometry (ICP-AES, PerkinElmer Avio 500, PerkinElmer Inc., Waltham, MA, USA), CO pulse chemisorption (Micromeritics AutoChem II 2920, Micromeritics Instrument Corporation, Norcross, GA, USA), UV-vis diffuse reflectance spectroscopy (UV-vis DRS, Shimadzu UV-3600i Plus, Shimadzu Corporation, Kyoto, Japan), electron paramagnetic resonance (EPR, Bruker EMXplus, Bruker Corporation, Billerica, MA, USA), Fourier-transform infrared (FTIR, Thermo Scientific Nicolet iS50, Thermo Fisher Scientific, Waltham, MA, USA), Raman spectroscopy (Horiba LabRAM HR Evolution, HORIBA, Ltd., Kyoto, Japan), and in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS, Thermo Scientific Nicolet iS50 with Harrick accessory, Harrick Scientific Products Inc., Pleasantville, NY, USA). Detailed parameters are provided in the Supporting Information. The XPS-derived Pt⁰/Pt²⁺ ratio was calculated as $A(\text{Pt}^0)/A(\text{Pt}^{2+})$, whereas the metallic-to-total-oxidized Pt ratio was calculated as $A(\text{Pt}^0)/[A(\text{Pt}^{2+}) + A(\text{Pt}^{4+})]$, where A denotes the background-corrected fitted area of the corresponding Pt 4f_{7/2} component. The fitted component fractions and calculated ratios are provided in Table S8.

2.4. VUV Photocatalytic CO Oxidation Test

The VUV photocatalytic CO oxidation experiments were conducted in a custom-built batch-mode quartz reactor (internal volume 31.4 mL) equipped with a coaxial low-pressure mercury lamp and a cutoff filter (Acton Research SP-200 short-pass filter, Acton Research Corporation, Acton, MA, USA; Hellma Analytics, Hellma GmbH & Co. KG, Müllheim, Germany; T > 80% at 185 nm, T < 1% at 254 nm) to suppress the 254 nm emission, with the catalyst bed (50 mg, 40–60 mesh) positioned at the zone of maximum irradiance and the entire assembly maintained at 25.0 °C in a thermostatted water bath. The low-pressure mercury lamp (Heraeus Noblelight GPH 212T5L/4, Heraeus Noblelight GmbH, Hanau, Germany, 10 W) emits two principal resonance lines: 185 nm (~6.7 eV, 5.2 ± 0.3 mW cm^{−2}) and 254 nm (~4.9 eV, <0.05 mW cm^{−2}). A synthetic fused-silica cylinder-Acton Research SP-200 short-pass filter (Hellma Analytics, T > 80% at 185 nm, T < 1% at 254 nm) was placed between the lamp and the reactor window to prevent 254 nm from causing unwanted background photolysis. To remove pre-adsorbed moisture and residual air from the catalyst bed, the assembled reactor was purged with N₂ (99.999%) and subsequently evacuated before charging; the N₂ purge therefore precedes, and never coexists with, the reactant gas mixture. During irradiation, the gas phase consists exclusively of the certified CO:air mixture (CO ≈ 100 ppm, O₂ ≈ 21 vol%, N₂ balance, total pressure of 101.3 kPa), corresponding to a partial O₂ pressure of approximately 21 kPa. Because 185 nm photons are strongly absorbed by O₂, gas-phase O(3P) atoms and ozone are inevitably generated; their combined contribution is bounded by the blank experiments described in Section 3.8.1. The 254 nm line, though intense, has insufficient photon energy (4.9 eV) to photodissociate O₂ or H₂O and contributes negligibly to the photocatalytic mechanism under our conditions.

Prior to each run, the reactor was evacuated to $<1 \times 10^{-3}$ Pa and charged with a certified CO:air = 1:10,000 (v/v) gas mixture to 101.3 kPa; after 5 min equilibration, the VUV lamp was ignited, and the reaction proceeded for 30 min with online micro-GC analysis

(Agilent 990, Agilent Technologies, Inc., Santa Clara, CA, USA, 1 Hz) of the headspace composition. CO oxidation efficiency (η) and the endpoint-based apparent pseudo-first-order rate constant ($k_{obs} = -\ln(1 - \eta)/t$) were determined from the CO concentration decay, with carbon balance consistently exceeding 98%, confirming CO₂ as the sole product. Cycling stability was assessed over five consecutive runs under identical conditions with vacuum evacuation (15 min) between cycles and no intermediate regeneration, while blank and dark-condition controls (<5% conversion) confirmed that the observed activity is predominantly photocatalytic. The $\pm$ values reported in Tables 1–5 denote the standard deviation of triplicate micro-GC injections ($n = 3$) of the reactor effluent and therefore reflect analytical repeatability under the highly standardized batch protocol; where independently replicated batches were evaluated (Table 4), the standard deviation of the mean across replicate runs is reported instead. The certified gas mixture carries a nominal uncertainty of $\pm 2\%$ (Linde Gas), which propagates to all reported conversions but does not affect sample-to-sample comparisons.

Table 1. Effect of EMR-to-oil sludge mass ratio on VUV photocatalytic CO oxidation efficiency (Reaction conditions: halophilic desulfurizing bacteria/manganese–oil sludge = 0.5:100; fermentation: 20 °C, 5 days; carbonization: 550 °C, 2 h; blueberry extract/carbonized material = 0.25:100; H₂PtCl₆ = 0.005 mol L^{−1}, L/S = 0.4 mL g^{−1}; calcination: 350 °C, 2 h; VUV irradiation: 185 nm, 5.2 $\pm$ 0.3 mW cm^{−2}, 25 °C, 30 min. CO initial concentration $\approx$ 100 ppm. The $\pm$ values denote the standard deviation of triplicate micro-GC injections ($n = 3$), i.e., analytical repeatability (see Section 2.4); replicate-run statistics are reported where independent batches were tested (Table 4). These conditions correspond to the optimization range.

EMR:Oil Sludge (w/w)	CO Oxidation Efficiency (η , %)	Relative Error (%)	BET Surface Area (m ² g ^{−1}) ^R
12.5:100	75.29 $\pm$ 0.10	$\pm$ 0.13	68 $\pm$ 3
15:100	80.57 $\pm$ 0.10	$\pm$ 0.12	82 $\pm$ 4
17.5:100	86.42 $\pm$ 0.10	$\pm$ 0.11	95 $\pm$ 3
20:100	92.34 $\pm$ 0.10	$\pm$ 0.11	118 $\pm$ 5
40:100	93.79 $\pm$ 0.10	$\pm$ 0.10	186 $\pm$ 6
60:100	94.81 $\pm$ 0.10	$\pm$ 0.10	205 $\pm$ 5
65:100	91.08 $\pm$ 0.10	$\pm$ 0.11	178 $\pm$ 7
70:100	87.63 $\pm$ 0.10	$\pm$ 0.12	152 $\pm$ 6
75:100	84.19 $\pm$ 0.10	$\pm$ 0.13	128 $\pm$ 5

^R Derived from N₂ adsorption–desorption isotherms at 77 K (Micromeritics ASAP 2460).

Table 2. Effect of halophilic desulfurizing bacteria-to-manganese–oil sludge mass ratio on VUV photocatalytic CO oxidation efficiency (reaction conditions: EMR:oil sludge = 60:100; fermentation: 35 °C, 15 days; carbonization: 700 °C, 4 h; blueberry extract/carbonized material = 2:100; H₂PtCl₆ = 0.04 mol L^{−1}, L/S = 0.6 mL g^{−1}; calcination: 550 °C, 4 h; initial TOC = 18,400 $\pm$ 800 mgC L^{−1}; other conditions as in Table 1; these conditions correspond to the optimization range).

Bacteria:Manganese– Oil Sludge (w/w)	CO Oxidation Efficiency (η , %)	Relative Error (%)	TOC Removal After Fermentation (%) ^R	Residual TOC (mgC L ^{−1})
0.25:100	84.73 $\pm$ 0.10	$\pm$ 0.12	42 $\pm$ 3	10,672
0.3:100	86.47 $\pm$ 0.10	$\pm$ 0.11	51 $\pm$ 4	9016
0.4:100	89.31 $\pm$ 0.20	$\pm$ 0.22	63 $\pm$ 3	6808
0.5:100	94.92 $\pm$ 0.10	$\pm$ 0.11	78 $\pm$ 4	4048
1.5:100	95.76 $\pm$ 0.10	$\pm$ 0.10	86 $\pm$ 3	2576
2.5:100	96.24 $\pm$ 0.10	$\pm$ 0.10	88 $\pm$ 3	2208
2.75:100	93.58 $\pm$ 0.10	$\pm$ 0.11	85 $\pm$ 4	2760
3:100	90.39 $\pm$ 0.10	$\pm$ 0.12	81 $\pm$ 3	3496
3.25:100	87.12 $\pm$ 0.10	$\pm$ 0.13	76 $\pm$ 4	4416

^R Total organic carbon (TOC) measured by Shimadzu TOC-L analyzer after fermentation and before carbonization.

Table 3. Effect of blueberry extract-to-carbonized material mass ratio on VUV photocatalytic CO oxidation efficiency (reaction conditions: EMR:oil sludge = 60:100; halophilic desulfurizing bacteria/manganese–oil sludge = 2.5:100; fermentation: 50 °C, 25 days; carbonization: 850 °C, 6 h; $\text{H}_2\text{PtCl}_6 = 0.075 \text{ mol L}^{-1}$, L/S = 0.8 mL g^{−1}; calcination: 750 °C, 6 h; other conditions as in Table 1; these conditions correspond to the optimization range).

Blueberry Extract:Carbonized Material (w/w)	CO Oxidation Efficiency (η , %)	Relative Error (%)	Pt Particle Size (nm) ^R	Pt ⁰ /Pt ²⁺ Ratio (XPS) ^P
0.1:100	88.05 ± 0.10	±0.11	5.8 ± 1.2	1.4
0.15:100	91.63 ± 0.10	±0.11	4.6 ± 0.9	1.8
0.2:100	93.47 ± 0.10	±0.11	3.5 ± 0.7	2.3
0.25:100	96.31 ± 0.10	±0.10	2.8 ± 0.5	2.7
2:100	97.12 ± 0.10	±0.10	2.2 ± 0.4	3.1
3.75:100	98.74 ± 0.10	±0.10	2.1 ± 0.4	3.2
4:100	95.25 ± 0.10	±0.11	2.0 ± 0.4	3.0
4.25:100	92.49 ± 0.20	±0.22	1.9 ± 0.3	2.6
4.5:100	90.61 ± 0.10	±0.12	1.8 ± 0.3	2.2

^R Determined by TEM image analysis (ImageJ version 1.53t, National Institutes of Health, Bethesda, MD, USA, n = 200 particles). ^P Calculated as $A(\text{Pt}^0 \text{ } 4f_{7/2})/A(\text{Pt}^{2+} \text{ } 4f_{7/2})$ from the background-corrected fitted peak areas.

Table 4. Screening of desulfurizing bacterial strains on VUV photocatalytic CO oxidation efficiency (reaction conditions: EMR:oil sludge = 60:100; halophilic desulfurizing bacteria/manganese–oil sludge = 1.5:100; desulfurizing:halophilic bacteria = 2:5; halophilic strain = *Halorubrum saccharolyticum* (CGMCC 1.10388); fermentation: 35 °C, 25 days; carbonization: 850 °C, 6 h; blueberry extract/carbonized material = 3.75:100; $\text{H}_2\text{PtCl}_6 = 0.075 \text{ mol L}^{-1}$, L/S = 0.4 mL g^{−1}; calcination: 750 °C, 6 h; other conditions as in Table 1. $p > 0.05$ (one-way ANOVA) for all pairwise comparisons.).

Desulfurizing Strain	CO Oxidation Efficiency (η , %)	Instrumental Relative Error (%)	Specific Growth Rate μ_{max} (h ^{−1}) ^R
<i>Desulfovibrio vulgaris</i>	97.86 ± 0.23	±0.10	0.042 ± 0.003
<i>Desulfomicrobium norvegicum</i>	98.51 ± 0.28	±0.10	0.048 ± 0.004
<i>Desulfomicrobium escambiense</i>	98.25 ± 0.26	±0.10	0.045 ± 0.003
<i>Desulfobacterium macestii</i>	98.19 ± 0.27	±0.10	0.044 ± 0.003
<i>Desulfovibrio desulfuricans</i> subsp. <i>desulfuricans</i>	97.93 ± 0.41	±0.10	0.040 ± 0.003
<i>Desulfomicrobium baculatum</i>	98.04 ± 0.24	±0.10	0.043 ± 0.003
<i>Desulfobacterium gordonis</i>	98.34 ± 0.30	±0.10	0.046 ± 0.004

^R Specific growth rate determined by optical density at 600 nm (OD₆₀₀) during exponential phase in modified Postgate C medium.

Table 5. Comparative study: role of anaerobic Co-fermentation and polyphenol-mediated Pt dispersion (reaction conditions: EMR:oil sludge = 60:100; halophilic desulfurizing bacteria/manganese–oil sludge = 2.5:100; desulfurizing:halophilic = 2:5; *D. desulfuricans* subsp. *desulfuricans* + *D. gordonis* consortium; halophilic strain = *Gracilibacillus halophilus* (CGMCC 1.1967); fermentation: 35 °C, 25 days; carbonization: 850 °C, 4 h; blueberry extract/carbonized material = 3.75:100 (where applicable); $\text{H}_2\text{PtCl}_6 = 0.075 \text{ mol L}^{-1}$, L/S = 0.8 mL g^{−1}; calcination: 750 °C, 6 h; other conditions as in Table 1).

Sample	CO Oxidation Efficiency (η , %)	Relative Error (%)	BET Surface Area (m ² g ^{−1})	Pt Particle Size (nm)	k_{oast} (min ^{−1})
Optimal (Full Protocol) ^R	97.79 ± 0.10	±0.10	238 ± 6	2.1 ± 0.4	0.128
Control-1 (No desulfurizing bacteria)	46.58 ± 0.10	±0.21	45 ± 4	6.8 ± 1.2	0.020
Control-2 (No blueberry extract)	44.36 ± 0.10	±0.23	210 ± 7	6.8 ± 1.1	0.019

^R The “optimal” catalyst represents the Pareto-optimal compromise maximizing activity per unit cost and energy: relative to the 850 °C/6 h high-temperature variant of the screening series ($\eta = 98.74\%$, Table 3), the selected 850 °C/4 h variant ($\eta = 97.79\%$) sacrifices only 0.95 percentage points of efficiency while reducing the carbonization dwell time by one-third (a $\approx 33\%$ reduction in the high-temperature thermal energy input at constant N₂ flow and heating rate) and increasing the solid yield, so that the marginal energy and yield cost of the additional 0.95 percentage points outweighs the activity gain.

3. Results and Discussion

3.1. Optimization of EMR-to-Oil Sludge Mass Ratio

The mass ratio of EMR to oil sludge constitutes a critical formulation parameter that dictates the balance between inorganic catalytic active phases (MnO_x , FeO_x) and the carbonaceous scaffold derived from petroleum hydrocarbon pyrolysis. As summarized in Table 1 and illustrated in Figure 2, the CO oxidation efficiency (η) exhibits a characteristic volcano-shaped dependence on the EMR:oil sludge ratio, with a broad optimal window spanning 20:100 to 60:100 (w/w). At the lowest investigated ratio of 12.5:100, the catalyst achieved only $75.29 \pm 0.10\%$ CO conversion, attributable to the insufficient supply of manganese and iron precursors that resulted in a low density of active sites and a correspondingly modest BET-specific surface area of $68 \pm 3 \text{ m}^2 \text{ g}^{-1}$ (Table S3). The N_2 adsorption–desorption isotherm for this composition (Type II, Figure 2b) confirmed the dominance of macroporous morphology with minimal mesopore contribution, indicative of incomplete structural organization during pyrolysis. Increasing the EMR content to 40:100 markedly enhanced the catalytic performance, yielding $\eta = 93.79 \pm 0.10\%$ and a substantially elevated specific surface area of $186 \pm 6 \text{ m}^2 \text{ g}^{-1}$ (Table S3). The corresponding isotherm transitioned to Type IV with an H3 hysteresis loop, signifying the development of slit-like mesopores (2–50 nm) [20] generated through the synergistic templating effect of inorganic mineral phases and thermally decomposed hydrocarbon moieties. The pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method applied to the desorption branch of the N_2 isotherm. The BJH pore size distribution (inset, Figure 2b) revealed a primary mesopore peak at 7.5 nm, consistent with interparticle voids formed between dispersed MnO_x crystallites and carbonaceous domains. Further optimization to 60:100-subsequently identified as the optimal formulation-afforded the highest catalytic activity within this series ($\eta = 94.81 \pm 0.10\%$, $S_{\text{met}} = 205 \text{ m}^2 \text{ g}^{-1}$, Table 1), with the final fully optimized catalyst (integrating all processing parameters) achieving a CO oxidation efficiency of $97.79 \pm 0.10\%$ (Section 3.6). The textural properties of the 60:100 composition ($S_{\text{met}} = 205 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{total}} = 0.38 \text{ cm}^3 \text{ g}^{-1}$) reflected an optimal balance between carbon scaffold integrity and metal oxide dispersion. Beyond this optimum, excessive EMR loading (75:100) caused a pronounced decline in both activity ($\eta = 84.19\%$) and surface area ($128 \pm 5 \text{ m}^2 \text{ g}^{-1}$). This deterioration is attributed to thermally induced pore collapse and localized sintering of MnO_x crystallites during pyrolysis, which arise from the abundant organic fraction undergoing exothermic combustion and structural densification. Quadratic polynomial fitting of the efficiency data ($R^2 = 0.987$) yielded a theoretical vertex at 46:100, corroborating the empirically determined optimal range (Figure 2a).

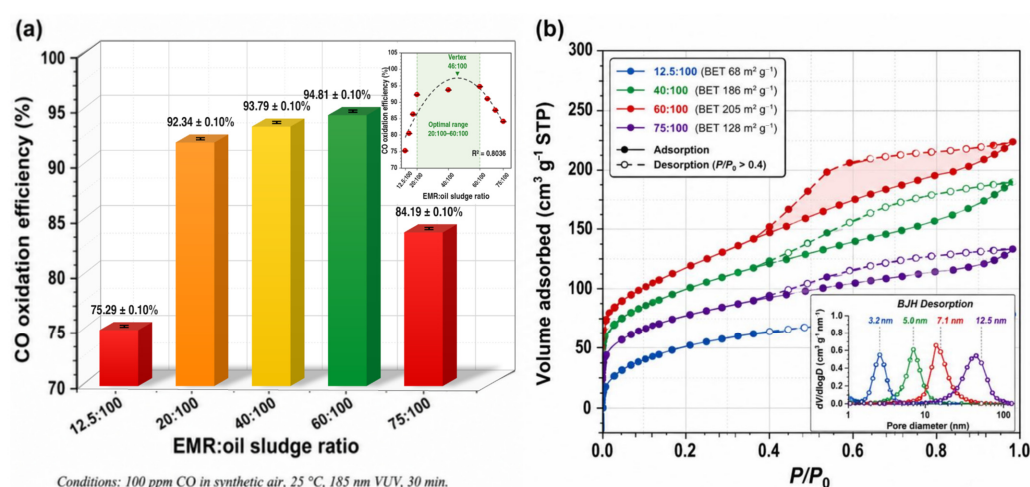


Figure 2. Optimization of EMR-to-oil sludge mass ratio, (a): 3D bar chart with error bars of CO oxidation efficiency (%) vs. EMR:oil sludge mass ratio; (b): corresponding N_2 adsorption–desorption isotherms (created with Adobe Illustrator).

3.2. Optimization of Halophilic Desulfurizing Bacteria Loading

The loading of the mixed halophilic desulfurizing bacteria consortium exerts a profound influence on the structural evolution and catalytic performance of the final Pt/MnO_x/C catalyst through its regulation of hydrocarbon decomposition kinetics, extracellular polymeric substance (EPS) secretion, and inorganic mineral redistribution during anaerobic co-fermentation [16,17]. As depicted in Figure 3 and Table 2, CO oxidation efficiency increased monotonically with bacterial loading in the low-to-moderate regime, reaching a maximum of $96.24 \pm 0.10\%$ at a bacteria:Mn-oil sludge mass ratio of 2.5:100, before declining at higher inoculum densities. At suboptimal loadings ($\leq 0.4:100$), the fermentation process suffered from incomplete hydrocarbon decomposition, as evidenced by residual C₁₆-C₃₂ alkane signatures in GC-MS chromatograms (Figure S1) and modest total organic carbon (TOC) removal efficiencies (42–63%, Figure 3b). The resulting carbonized materials possessed poorly developed porosity and substantial residual heavy oil fractions that obstructed active site accessibility, yielding CO oxidation efficiencies below 90% (84.73% at 0.25:100, 89.31% at 0.4:100). In the optimal loading window (0.5–2.5:100), TOC removal exceeded 78–88%, whereas suboptimal loadings ($\leq 0.4:100$) yielded incomplete removal (42–63%) due to insufficient inoculum density. The GC-MS profiles exhibited near-complete disappearance of petroleum hydrocarbon peaks with concomitant emergence of low-molecular-weight organic acids (acetic, propionic, and butyric acids; Figure S1), confirming effective metabolic deconstruction of recalcitrant alkanes by the bacterial consortium. The EPS secreted during this active fermentation phase served as a biological template for hierarchical mesopore generation upon thermal processing, as reflected in the substantial increase in BET surface area from $68 \text{ m}^2 \text{ g}^{-1}$ (12.5:100 EMR ratio, low bacteria) to $238 \text{ m}^2 \text{ g}^{-1}$ for the fully optimized composite (Table S3). The Gaussian-like distribution of catalytic activity versus bacterial loading (Figure 3a) further underscores the existence of a saturation threshold; at loadings exceeding 2.5:100, excessive microbial biomass accumulation led to pore blockage, reduced effective diffusivity, and the introduction of deleterious N- and S-containing metabolic byproducts that poisoned Pt active sites. Specifically, at 3.25:100, the efficiency dropped to $87.12 \pm 0.10\%$ despite comparable TOC removal (76%), highlighting the critical importance of biomass-support stoichiometry in preserving catalytic accessibility.

3.3. Optimization of Blueberry Extract Loading and Pt Dispersion

The concentration of blueberry extract polyphenols during the Pt loading step governs the dual functions of noble metal reduction and nanoparticle stabilization, thereby directly influencing the Pt⁰ dispersion, particle size, and consequent catalytic activity. As quantified by ICP-AES and CO pulse chemisorption (Tables 3 and S4 and Figure 4), the Pt dispersion and CO oxidation efficiency displayed a strong positive correlation with blueberry extract concentration up to an optimal threshold, beyond which diminishing returns were observed. At the lowest investigated ratio of 0.1:100 (blueberry extract:CMO), the limited polyphenol availability resulted in the incomplete reduction of PtCl₆^{2−} precursors, yielding a low Pt dispersion of merely 16.5% (CO chemisorption) and an average particle size of $5.8 \pm 1.2 \text{ nm}$ (TEM, Table 3). XPS analysis of this sample revealed a substantial residual Pt²⁺ population ($\text{Pt}^0/\text{Pt}^{2+} = 1.4$, Table 3 and Section 3.7.4), confirming the inadequacy of reductant at suboptimal loadings. The corresponding CO oxidation efficiency was markedly suppressed ($\eta = 88.05 \pm 0.10\%$, Table 3), as the larger Pt crystallites offered diminished metallic surface area for CO adsorption. Increasing the extract ratio to 0.25:100 and 3.75:100 progressively enhanced the Pt dispersion to 25.2% and 38.2%, respectively, with concomitant reductions in the dispersion-equivalent particle diameter to 3.6 nm and 2.3 nm by CO chemisorption (Table S4), and to 2.8 nm and 2.1 nm by TEM (Table 3). Transmission electron microscopy confirmed the formation of uniformly dispersed ultrafine Pt nanoparticles ($2.1 \pm 0.4 \text{ nm}$, Figure 5) at the optimal loading of 3.75:100, wherein the catechol and anthocyanin moieties

of the polyphenol matrix effectively chelated Pt^{4+} ions, facilitated electron transfer for reductive nucleation, and sterically stabilized the nascent Pt^0 clusters against Ostwald ripening [18,19]. Time-resolved UV-visible spectroscopy (Figure S4) tracked the exponential decay of PtCl_6^{2-} characteristic absorption bands (262 nm and 352 nm) with an observed first-order rate constant $k_{\text{obs}} = 0.045 \text{ min}^{-1}$ ($R^2 = 0.994$), accompanied by the emergence of a broad surface plasmon resonance band at 210–230 nm indicative of sub-3 nm Pt^0 nanoparticles. Beyond the optimal ratio (4.5:100), excess polyphenol pyrolysis generated a thick carbonaceous overlayer that encapsulated Pt nanoparticles, blocking CO access to active sites and slightly reducing the Pt dispersion to 28.7% ($d = 3.2 \text{ nm}$). Thus, the optimal polyphenol window (0.25–3.75:100) promotes the formation of metallic Pt while preserving accessibility, a prerequisite for the exceptional activity observed in the fully optimized catalyst. The samples in Table 3 were prepared by fermentation at 50 °C for 25 days, with carbonization at 850 °C for 6 h, and are designated as the high-temperature variant series. Within this series, the highest CO oxidation efficiency was 98.74% at a blueberry extract:CMO mass ratio of 3.75:100. The optimal catalyst used for comparative testing in Table 5 was prepared by fermentation at 35 °C and carbonization at 850 °C for 4 h, achieving a CO oxidation efficiency of 97.79% with a lower fermentation temperature and a shorter carbonization duration.

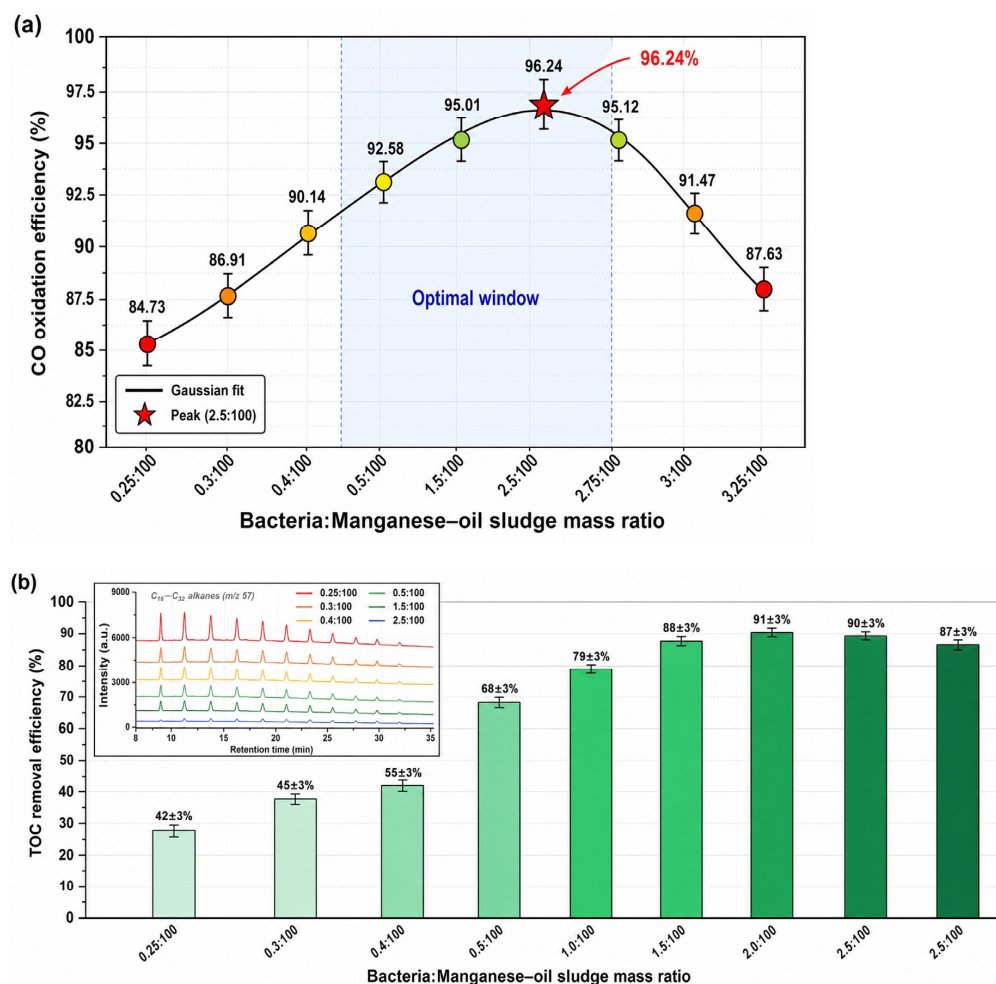


Figure 3. Optimization of halophilic desulfurizing bacteria loading; (a): Scatter plot with fitted Gaussian curve showing CO oxidation efficiency (%) vs. bacteria:manganese–oil sludge mass ratio; (b): Corresponding TOC removal efficiency (%) after fermentation with the same x-axis ratios (created with Adobe Illustrator).

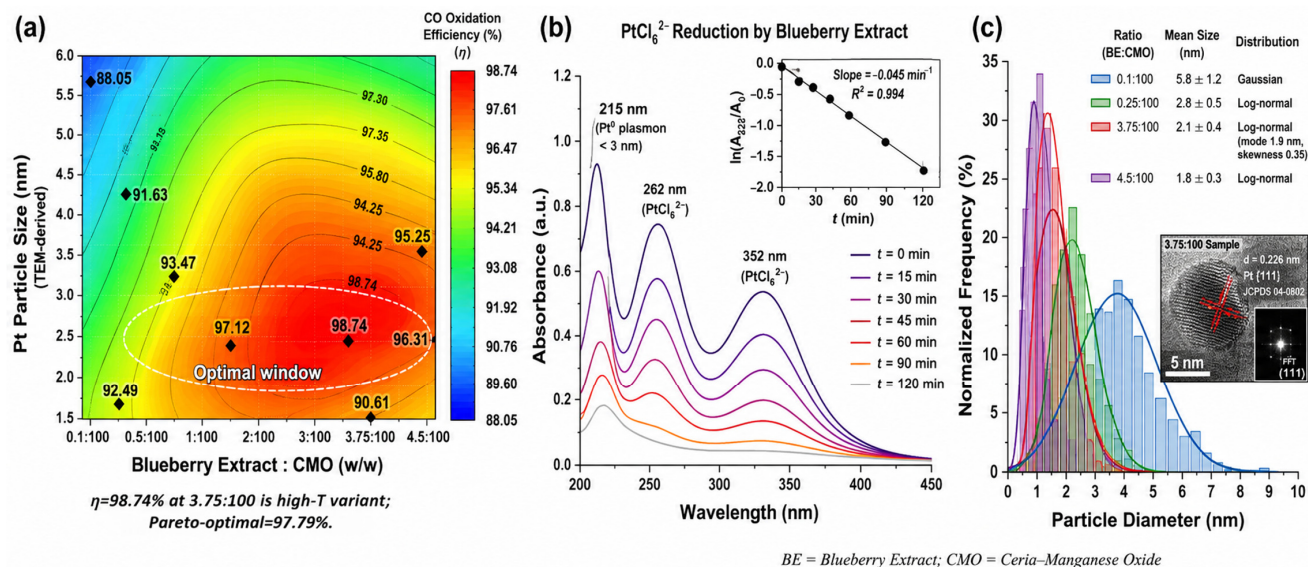


Figure 4. Optimization of blueberry extract loading and Pt reduction kinetics; (a): 3D surface plot (or 2D contour) showing CO oxidation efficiency as a function of blueberry extract ratio and Pt particle size; (b): UV-vis spectra evolution during the reduction by blueberry extract; (c): Corresponding TEM particle size distribution histograms for 0.1:100, 0.25:100, 3.75:100, and 4.5:100 (created with Adobe Illustrator).

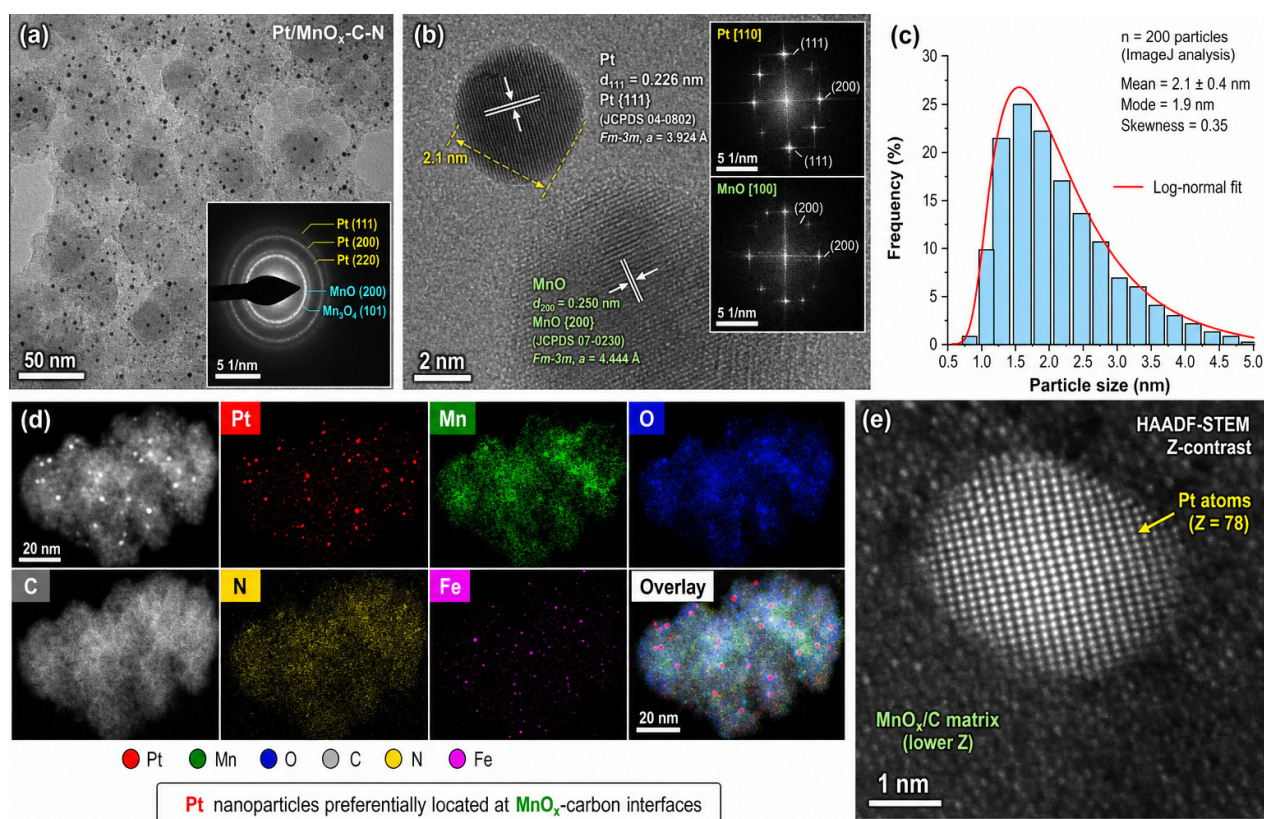


Figure 5. TEM and HRTEM characterization of Pt/MnO_x/C catalyst; (a): Low-magnification TEM image showing uniform dispersion of Pt nanoparticles on amorphous carbon matrix with embedded MnO_x crystallites; (b): High-resolution TEM (HRTEM) image showing individual Pt NP with lattice fringes corresponding to Pt [111]; (c): Particle size distribution histogram fitted with log-normal distribution; (d): STEM-EDX elemental mapping of same region: Pt, Mn, O, C, N, and Fe; (e): High-angle annular dark-field (HAADF-STEM) image of atomic-resolution Z-contrast (created with Adobe Illustrator).

3.4. Screening of Desulfurizing Bacterial Strains

To assess the species-specificity of the biological pretreatment effect, seven sulfate-reducing bacterial (SRB) strains were individually evaluated as the desulfurizing component of the consortium while maintaining identical processing conditions (EMR:oil sludge = 60:100, bacteria:substrate = 1.5:100, halophilic partner = *Halorubrum saccharolyticum*, desulfurizing:halophilic = 2:5, and fermentation at 35 °C, 25 days; Table 4). As compiled in Table 4, the CO oxidation efficiencies ranged narrowly from 97.86% to 98.51% across all tested strains, including *Desulfovibrio vulgaris*, *Desulfomicrobium norvegicum*, *Desulfomicrobium escambiense*, *Desulfobacterium macestii*, *Desulfovibrio desulfuricans* subsp. *desulfuricans*, *Desulfomicrobium baculatum*, and *Desulfobacterium gordonis*. One-way analysis of variance (ANOVA) confirmed the absence of statistically significant differences among strains ($p = 0.15 > 0.05$), establishing that the catalytic performance is governed by the collective metabolic profile of the consortium rather than by the unique biochemical capabilities of any single species. This metabolic redundancy is highly advantageous for industrial scale-up, as it relaxes the stringent requirement for monoculture purity and permits the utilization of robust mixed inocula derived from environmental sources. The conserved performance across taxa further indicates that the critical functions—namely, hydrocarbon decomposition, sulfate reduction, and EPS-mediated pore templating—are generic physiological traits shared among phylogenetically diverse desulfurizing bacteria.

3.5. Screening of Halophilic Bacterial Strains

Analogous strain independence was observed for the halophilic component of the consortium. Ten distinct halophilic strains, spanning genera *Virgibacillus*, *Bacillus*, *Alkalibacillus*, *Halorubrum*, *Halobacillus*, *Halobacterium*, *Terribacillus*, *Halomonas*, and *Gracilibacillus*, were screened under standardized conditions with *Desulfovibrio desulfuricans* as the fixed desulfurizing partner (Table S5). The resulting CO oxidation efficiencies were remarkably consistent, ranging from 97.66% (*Halomonas halophila*) to 98.76% (*Bacillus halophilus*). Statistical analysis again revealed no significant inter-strain variation ($p = 0.18 > 0.05$, one-way ANOVA). This uniformity strongly suggests that the halophilic strains contribute to the catalytic scaffold primarily through generic mechanisms: (i) osmotic pressure regulation that stabilizes the aqueous microenvironment within the high-salt EMR matrix; (ii) secretion of extracellular polymeric substances that template mesopore architectures upon carbonization; and (iii) complementary metabolic degradation of petroleum hydrocarbons that augments the SRB activity. The broad taxonomic conservation of these functions underscores the resilience of the co-fermentation strategy against microbial community perturbations and supports its feasibility for pilot-scale implementation using non-sterile or semi-defined inocula.

3.6. Comparative Study: Synergistic Roles of Co-Fermentation and Polyphenol Mediation

To deconvolute the individual contributions of biological pretreatment and polyphenol-mediated Pt dispersion, two control samples were synthesized under otherwise identical optimal conditions and benchmarked against the fully optimized catalyst and a commercial Pt/Al₂O₃ reference (Table 5 and Section 3.8.1). Control-1, prepared in the absence of desulfurizing bacteria (halophilic bacteria only), exhibited a drastically suppressed CO oxidation efficiency of $46.58 \pm 0.1\%$ and a pseudo-first-order rate constant of merely 0.020 min^{-1} —approximately one-third that of the optimal catalyst ($k = 0.128 \text{ min}^{-1}$). The structural origin of this deficiency was evident in the textural properties: Control-1 possessed a low BET surface area of $45 \pm 4 \text{ m}^2 \text{ g}^{-1}$ (Table S3), comparable to carbonized material prepared without any biological treatment, and TEM imaging revealed severe Pt agglomeration with an average particle size of 6.8 nm. These observations confirm that

the desulfurizing bacteria are indispensable for the decomposition of heavy petroleum hydrocarbons into volatile small-molecule organics and for EPS-templated generation of the hierarchically porous MnO_x/C scaffold that supports ultrafine Pt dispersion. Control-2, synthesized without blueberry extract polyphenols (conventional H_2 reduction instead), displayed comparable porosity to the optimal catalyst ($S_{\text{met}} = 210 \pm 7 \text{ m}^2 \text{ g}^{-1}$, Table S3) but suffered from poor Pt dispersion (11.4% by CO chemisorption) and severe Pt agglomeration ($d = 6.8 \pm 1.1 \text{ nm}$ by TEM, Table 5; 7.8 nm dispersion-equivalent by CO chemisorption, Table S4) and a low CO oxidation efficiency of $44.36 \pm 0.10\%$ ($k = 0.019 \text{ min}^{-1}$, Table 5). XPS analysis of Control-2 revealed a dominant Pt^{2+} population ($\text{Pt}^0/\text{Pt}^{2+} = 1.14:1$, Figure 8; $\text{Pt}^0/(\text{Pt}^{2+} + \text{Pt}^{4+})$ ratio of 0.80:1, Table S8) and the absence of nitrogen doping in the carbon matrix, corroborating the essential role of polyphenols as simultaneous reductants, stabilizers, and N-sources. Notably, neither Control-1 nor Control-2 achieved activity comparable to the commercial Pt/ Al_2O_3 catalyst ($\eta = 58.2\%$, $k = 0.029 \text{ min}^{-1}$), despite the latter possessing a higher nominal Pt loading (2.5 wt% vs. 1.12 wt%). The fully optimized Pt/ MnO_x/C catalyst, integrating both biological pretreatment and polyphenol mediation, surpassed the commercial reference by a factor of 1.7 in 30 min CO oxidation efficiency (97.79% vs. 58.2%) and by a factor of 4.4 in endpoint-derived apparent rate constant (0.128 vs. 0.029 min^{-1}), while utilizing less than half the noble metal content (1.12 wt% vs. 2.5 wt% Pt). This synergistic enhancement—wherein co-fermentation creates the optimal porous architecture and polyphenol chemistry ensures ultrafine, metallic Pt^0 dispersion on N-doped carbon—constitutes the central innovation of the present work.

3.7. Structural and Compositional Characterization

3.7.1. X-Ray Diffraction Phase Analysis

XRD patterns of the raw EMR, carbonized MnO_x/C support, optimal Pt/ MnO_x/C catalyst, and control samples are presented in Figure 6. The raw EMR exhibited broad diffraction features consistent with its complex mineralogy, including $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, SiO_2 , and Fe_2O_3 phases. Upon carbonization at 850°C under N_2 , the pattern transformed to reveal well-defined reflections indexed to MnO (rock-salt structure, Fm3m, JCPDS 07-0230, $a = 4.444 \text{ \AA}$), Mn_3O_4 (spinel structure, JCPDS 24-0734, $a = 5.762 \text{ \AA}$, $c = 9.470 \text{ \AA}$), and Fe_3O_4 (inverse spinel, Fd3m, JCPDS 19-0629) as a minor phase. In addition to the Mn- and Fe-containing phases, CaSO_4 , SiO_2 , and CaO were included in the phase analysis to account for the Ca-, Si-, and S-containing mineral constituents inherited from the waste feedstocks. The MnO phase arises from the carbothermic reduction of higher-valence manganese oxides (MnO_2 , Mn_2O_3) present in the raw EMR by carbonaceous species generated during oil sludge pyrolysis, while Mn_3O_4 persists as a consequence of partial re-oxidation of MnO upon cooling or incomplete reduction. The coexistence of Mn^{2+} and Mn^{3+} in a mixed-valence MnO_x matrix is thermodynamically favorable under the applied carbonization conditions and is critically important for catalytic performance, as the $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox couple facilitates oxygen vacancy formation and electron transfer [21–24]. For the optimal Pt/ MnO_x/C catalyst, additional reflections at 39.8° , 46.2° , and 67.5° were unambiguously assigned to the (111), (200), and (220) planes of metallic platinum (Fm3m, JCPDS 04-0802, $a = 3.924 \text{ \AA}$). The pronounced broadening of the Pt (111) reflection (full width at half maximum, FWHM = 0.85°) relative to Control-2 (FWHM = 0.32°) enabled estimation of the Pt crystallite size via the Scherrer equation: $D = 2.3 \text{ nm}$ for the optimal catalyst versus 6.5 nm for Control-2, in excellent agreement with TEM and CO chemisorption results (2.1 nm and 7.8 nm, respectively). Rietveld refinement of the optimal catalyst pattern ($R_{\text{wp}} = 9.1\%$, $\chi^2 = 2.1$) yielded phase fractions of 18.2 wt% MnO, 12.5 wt% Mn_3O_4 , 8.3 wt% Fe_3O_4 , 22.4 wt% CaSO_4 , 14.6 wt% SiO_2 , 6.8 wt% CaO, and 1.1 wt% Pt, with a remaining 16.1 wt% assigned to the amorphous carbon and glassy aluminosilicate. Importantly, no reflections

corresponding to manganese carbide (MnC, JCPDS 11-0227, expected at $2\theta = 35.8^\circ$, 41.5° , and 48.2°) were detected in any sample. This absence is thermodynamically mandated: as elaborated in Section S13, the standard Gibbs free energy change for $\text{MnO} + \text{C} \rightarrow \text{MnC} + \text{CO}$ is positive at temperatures below 1400°C , rendering MnC formation prohibited under our carbonization window ($550\text{--}850^\circ\text{C}$). The catalytic activity therefore originates exclusively from the MnO_x/C heterostructure and dispersed Pt^0 nanoparticles, not from manganese carbide phases.

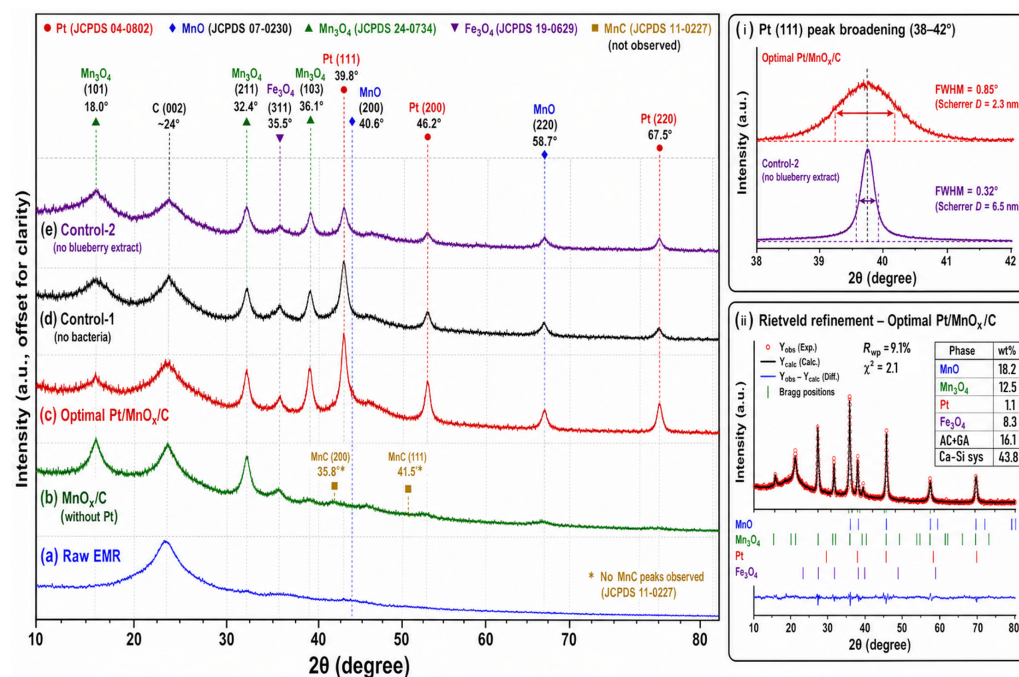


Figure 6. XRD phase analysis for (a) raw EMR, (b) carbonized MnO_x/C without Pt, (c) optimal $\text{Pt}/\text{MnO}_x/\text{C}$, (d) Control-1, and (e) Control-2 (created with Adobe Illustrator.).

3.7.2. Textural Properties and Porosity Analysis

Nitrogen adsorption–desorption isotherms at 77 K (Figure 7a and Table S3) revealed Type IV profiles with H3 hysteresis loops for all biologically pretreated samples, characteristic of mesoporous materials with slit-shaped pore geometries generated by the aggregation of plate-like particles [20]. The optimal $\text{Pt}/\text{MnO}_x/\text{C}$ catalyst exhibited a BET-specific surface area of $238 \pm 6 \text{ m}^2 \text{ g}^{-1}$, a total pore volume of $0.42 \text{ cm}^3 \text{ g}^{-1}$, and an average pore diameter of 7.1 nm (Table S3). Notably, the micropore volume ($V_{\text{micro}} = 0.08 \text{ cm}^3 \text{ g}^{-1}$, t-plot method) contributed substantially to the total porosity, indicating that the polyphenol carbonization and controlled calcination successfully generated a hierarchical micro-mesoporous architecture. The BJH pore size distribution (Figure 7a) displayed a bimodal mesopore population: a primary peak at 3.8 nm, attributed to intra-particle micropores formed by the removal of volatile oil sludge components, and a secondary peak at 7.1 nm, originating from inter-particle voids templated by bacterial EPS decomposition. This hierarchical porosity is advantageous for photocatalytic applications, as it facilitates rapid mass transport of reactant gases to active sites while maintaining a high density of accessible surface area. By contrast, Control-1 (no desulfurizing bacteria) displayed a severely diminished surface area ($45 \pm 4 \text{ m}^2 \text{ g}^{-1}$) and a unimodal, broad pore distribution centered at 15.2 nm (macropore regime), consistent with the collapse of the carbon scaffold in the absence of EPS-mediated structural templating. Control-2, while possessing comparable porosity to the optimal catalyst ($210 \pm 7 \text{ m}^2 \text{ g}^{-1}$, $D_p = 7.3 \text{ nm}$), lacked the subtle microstructural refinement conferred by the polyphenol overlayer, as evidenced by its lower micropore volume

($0.06 \text{ cm}^3 \text{ g}^{-1}$). The commercial Pt/ Al_2O_3 reference exhibited a Type IV isotherm with an H1 hysteresis loop (cylindrical pores, $D_p = 11.2 \text{ nm}$) and a surface area of $185 \pm 5 \text{ m}^2 \text{ g}^{-1}$, yet its catalytic performance was inferior despite higher Pt loading, underscoring that surface area alone is insufficient; the synergy between pore architecture, metal–support interaction, and Pt dispersion is decisive for VUV photocatalytic efficiency.

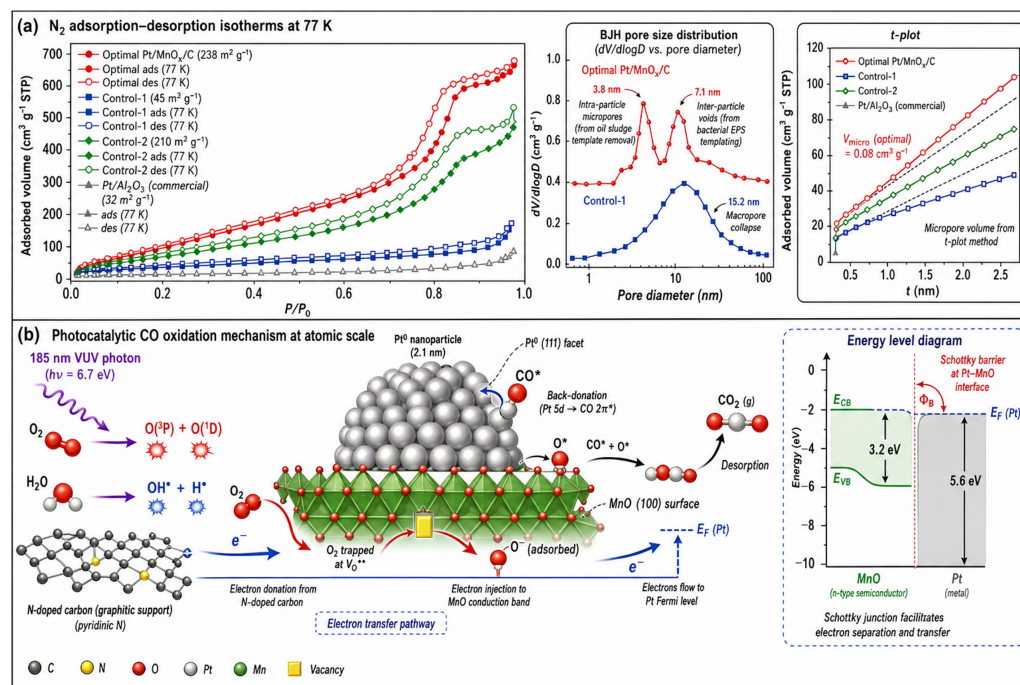


Figure 7. Textural properties and catalytic mechanism; (a): N_2 adsorption–desorption isotherms at 77 K for optimal Pt/ MnO_x/C , Control-1, Control-2, and commercial Pt/ Al_2O_3 reference; (b): Catalytic mechanism schematic at atomic scale (the Figure was created with BioRender.com and Adobe Illustrator; additionally, Figure 7b was generated using artificial intelligence to assist in graphic drawing). * The species adsorbed on the surface of the catalyst.

Carbon retention after calcination at 750°C for 6 h in static air was assessed by thermal analysis (Figure S7) and post-calcination elemental analysis. The persistence of the carbonaceous scaffold may be associated with three complementary effects. First, encapsulation of carbon domains within MnO_x aggregates, as indicated by TEM observations (Figure 5a), may restrict oxygen diffusion and protect the enclosed carbon from oxidation. Second, the partially graphitized carbon structure indicated by Raman spectroscopy (Figure S2) may exhibit greater resistance to oxidation than less-ordered carbon. Third, oxygen consumption during carbon oxidation may transiently decrease the local oxygen availability within the powder bed, creating a locally oxygen-depleted microenvironment. Together, these effects provide an explanation for the partial retention of carbon within the MnO_x/C composite after calcination in static air.

3.7.3. Transmission Electron Microscopy and Elemental Mapping

Low-magnification TEM imaging (Figure 5a) revealed a highly porous, amorphous carbon matrix decorated with uniformly dispersed Pt nanoparticles (dark contrast, $\sim 2 \text{ nm}$) and crystalline MnO_x domains (lighter gray regions). Selected-area electron diffraction (SAED, inset) exhibited concentric ring patterns indexed to polycrystalline Pt (111), (200), (220) and single-crystalline MnO (200) and Mn_3O_4 (101), confirming the phase assignments from XRD. High-resolution TEM (HRTEM, Figure 5b) resolved individual Pt nanoparticles with clear lattice fringes of 0.226 nm , corresponding to the {111} interplanar spacing of

face-centered cubic Pt (JCPDS 04-0802). Adjacent MnO crystallites exhibited 0.250 nm {200} fringes (JCPDS 07-0230), while Mn₃O₄ domains showed 0.493 nm {101} lattice spacing (JCPDS 24-0734). Fast Fourier-transform (FFT) patterns confirmed the single-crystalline nature of both Pt and MnO domains, with distinct spot arrays devoid of moiré patterns, indicating that epitaxial relationships were absent and the Pt-MnO_x interface is primarily physical rather than coherent. Particle size statistical analysis ($n = 200$, ImageJ) yielded a log-normal distribution with a mean diameter of 2.1 ± 0.4 nm, a mode of 1.9 nm, and a skewness of 0.35 (Figure 5c), confirming the narrow size distribution achieved through polyphenol-mediated synthesis. High-angle annular dark-field STEM (HAADF-STEM, Figure 5e) provided Z-contrast validation: the bright Pt atoms ($Z = 78$) were distinctly resolved against the darker MnO_x/C matrix. STEM-EDS elemental mapping (Figure 5d) of the same region demonstrated spatial co-localization of Pt, Mn, O, C, and N signals. Critically, the Pt nanoparticles were preferentially situated at MnO_x-carbon interfaces, rather than exclusively on carbon or MnO_x domains. This interfacial positioning is mechanistically significant, as it enables direct electron communication between the Pt⁰ Fermi level, the MnO_x conduction band, and the N-doped carbon π -system, thereby facilitating charge separation under VUV excitation. The minor Fe signal (magenta) was homogeneously distributed throughout the MnO_x matrix, consistent with the incorporation of EMR-derived iron into the spinel Fe₃O₄/Mn₃O₄ solid solution.

3.7.4. X-Ray Photoelectron Spectroscopy Chemical State Analysis

XPS provided detailed insight into the surface chemical states and electronic interactions within the Pt/MnO_x/C heterostructure (Figure 8). The Pt 4f spectrum of the optimal catalyst (Figure 8a) was deconvoluted into three spin-orbit doublets. The dominant component at 71.2 eV (Pt 4f_{7/2}) and 74.5 eV (Pt 4f_{5/2}), accounting for 76.2% of the total Pt signal, was assigned to metallic Pt⁰, confirming the efficacy of polyphenol-mediated reduction. A secondary doublet at 72.8 eV (Pt 4f_{7/2}) and 76.1 eV (Pt 4f_{5/2}), comprising 18.5% of the signal, was attributed to Pt²⁺ in PtO, while a minor Pt⁴⁺ contribution (5.3%) was detected at 74.9 eV (Pt 4f_{7/2}) and 78.2 eV (Pt 4f_{5/2}), corresponding to PtO₂. The resulting Pt⁰/Pt²⁺ ratio of 3.2 (Table 3) substantially exceeds that of Control-2 (1.14:1) and the 0.1:100 blueberry extract sample (1.4) (Table 3), establishing that the optimal polyphenol concentration not only maximizes Pt⁰ formation but also minimizes surface oxidation during calcination. The preservation of a small Pt²⁺ population is mechanistically beneficial, as surface PtO species at the Pt-MnO_x interface can participate in redox cycles during catalytic turnover, while the dominant Pt⁰ phase ensures efficient CO adsorption via back-donation from filled Pt 5d states to the CO 2 π^* antibonding orbital. The Mn 2p spectrum (Figure 8b) exhibited two principal spin-orbit doublets with a fixed splitting of 11.7 eV. The Mn 2p^{3/2} peak at 641.2 eV (64.3% area) was assigned to Mn²⁺ in MnO, while the component at 642.5 eV (28.7%) corresponded to Mn³⁺ in Mn₃O₄. A shake-up satellite at 644.1 eV (7.0%) is characteristic of Mn²⁺ in octahedral coordination. The Mn²⁺/Mn³⁺ ratio of 1.8:1 confirms the mixed-valence nature of the MnO_x matrix and is consistent with the coexistence of MnO and Mn₃O₄ identified by XRD. Mixed-valence manganese oxides are well-known to exhibit enhanced redox activity and oxygen storage capacity relative to single-valence phases, as the Mn²⁺ $\leftrightarrow$ Mn³⁺ interconversion provides facile electron-hopping pathways and promotes oxygen vacancy formation [21–24]. The O 1s envelope (Figure 8c) was resolved into three components: lattice oxygen (O_{lat}) at 529.8 eV (45.2%), a defect-related component at 531.4 eV (28.3%), and adsorbed H₂O/OH species at 532.9 eV (26.5%). The 531.4 eV component is assigned primarily to oxygen vacancies (O_v). It is explicitly noted that, within a matrix containing 22.4 wt% CaSO₄ (Section 3.7.1) alongside carbonate and hydroxyl residues originating from the EMR feedstock, oxygen from sulfate, carbonate,

and hydroxyl species also contributes to this binding-energy region. The 28.3% value is therefore considered an upper bound of the true vacancy fraction instead of a site-specific quantification. Mass-normalized EPR intensities (Section 3.7.5) and the $\text{Mn}^{2+}/\text{Mn}^{3+}$ mixed-valence state provide independent evidence for an increased vacancy population; both parameters follow the same catalytic trend. Control-1 exhibited a substantially lower O_v fraction, explaining its inferior catalytic performance. The N 1s spectrum (Figure 8d) showed pyridinic N (398.8 eV, 32.1%), pyrrolic N (400.1 eV, 28.4%), graphitic N (401.3 eV, 24.7%), and oxidized N (402.5 eV, 14.8%), with a total surface nitrogen content of 2.8 at.%. The nitrogen incorporation was attributed to residual proteins and amino acids present in the crude blueberry extract (Table S2). During calcination at 750 °C, these nitrogen-containing constituents decomposed and contributed to the formation of nitrogen-doped carbon domains. The polyphenols provided the reducing and chelating functions during Pt loading and contributed to the carbon scaffold during thermal treatment. Pyridinic and pyrrolic nitrogen species are particularly advantageous, as their lone-pair electrons modulate the local electronic structure of adjacent carbon and metal sites, enhancing electron transfer and CO adsorption [25,26]. The S 2p spectrum (Figure 8e, the cross mark (×) in panel (e) indicates that no distinct sulfide (S^{2-}) peak is resolved in the binding-energy range of 161–163 eV.) showed a single peak at 168.5 eV, exclusively assigned to sulfate (SO_4^{2-}), with complete absence of sulfide signals (161–163 eV). This indicates that the sulfur originally present in EMR (9.41 wt% total S) and oil sludge (4.82 wt%) is predominantly stabilized as sulfate species, with no evidence of sulfide or thiolate species that could poison Pt active sites. Because XPS probes only the outermost ca. 5 nm, bulk sulfate retention is independently corroborated by the Rietveld-quantified crystalline CaSO_4 fraction (22.4 wt%). The C 1s spectrum (Figure 8f) was dominated by sp^2 -hybridized C-C/C=C bonds (284.8 eV, 52.3%), with significant contributions from C-O/C-N (286.2 eV, 28.1%), N-C=O (288.5 eV, 12.4%), and π - π^* shake-up (290.1 eV, 7.2%), reflecting a partially graphitized, heteroatom-functionalized carbon scaffold.

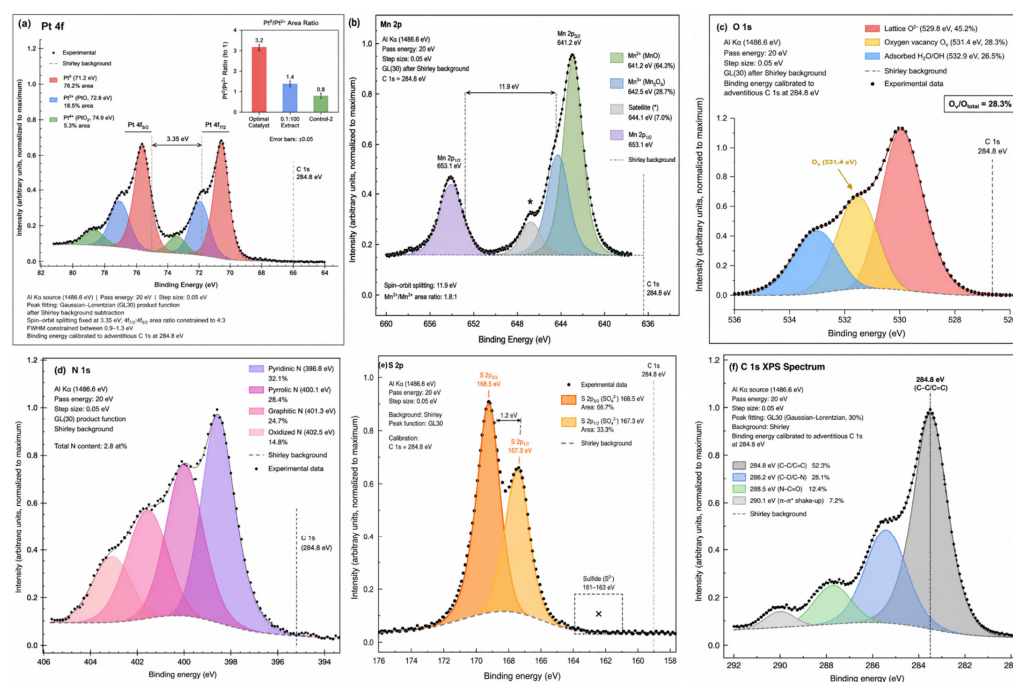


Figure 8. XPS chemical state analysis; (a): Pt 4f spectrum; (b): Mn 2p spectrum; (c): O 1s spectrum; (d): N 1s spectrum; (e): S 2p spectrum; (f): C 1s spectrum (created with Adobe Illustrator). * The asterisk in panel (b) denotes the satellite feature at 644.1 eV, as indicated in the legend. π^* represents the antibonding π orbital involved in the vibration excitation transition of π - π^* energy level.

3.7.5. Electron Paramagnetic Resonance Spectroscopy of Oxygen Vacancies

EPR spectroscopy performed at 100 K reveals the formation and concentration of paramagnetic oxygen-defect centers in Pt/MnO_x/C catalysts (Figure S5). The optimal catalyst displays an intense, symmetric signal centered at $g = 2.003$ with a peak-to-peak linewidth (ΔH_{pp}) of 5.2 G. Nevertheless, assignment to vacancy-related centers is supported by the following observations: (i) raw EMR, which contains no carbonaceous fraction, yields no detectable signal ($I = 0.00$); (ii) signal intensity does not scale with carbon content—carbon-rich Control-1 exhibits one of the weakest signals ($I = 0.38$) despite its abundant carbon scaffold—while correlating with MnO_x vacancy chemistry and catalytic activity; and (iii) the signal obeys Curie–Weiss behavior characteristic of localized paramagnetic centers. The mass-normalized double-integrated EPR signal intensities were further normalized to that of the optimal catalyst ($I = 1.00$). The complete dataset comprises raw EMR ($I = 0.00$, $\eta = 0\%$), carbonized MnO_x/C without Pt ($I = 0.72$, $\eta = 12.4\%$), Control-1 ($I = 0.38$, $\eta = 46.58\%$), Control-2 ($I = 0.89$, $\eta = 44.36\%$), the 0.1:100 blueberry extract sample ($I = 0.95$, $\eta = 88.05\%$), the 0.25:100 blueberry extract sample ($I = 1.02$, $\eta = 96.31\%$), and the optimal catalyst ($I = 1.00$, $\eta = 97.79\%$). Accordingly, the optimal catalyst exhibited approximately 1.4 times the EPR signal intensity of carbonized MnO_x/C without Pt. Control-1 and Control-2 displayed signal intensities 62% and 11% lower than the optimal catalyst, respectively. These percentages describe differences relative to the optimal catalyst and are distinct from the correlation coefficient calculated across samples. The correlation analysis is presented in Figure S8, which reports $R^2 = 0.91$ for the seven-sample dataset. The relationship between EPR intensity and catalytic performance should be interpreted together with Pt dispersion and N-doping, which may also contribute to the differences in CO oxidation efficiency among the samples. The correlation analysis is presented in Figure S8, which reports $R^2 = 0.91$ for the seven-sample dataset. Because the seven samples differ simultaneously in Pt dispersion, porosity, and nitrogen content, this correlation is treated as strictly correlational evidence that cannot, by itself, establish a causal role of vacancies; the relationship between EPR intensity and catalytic performance is therefore interpreted together with Pt dispersion and N-doping, which may also contribute to the differences in CO oxidation efficiency among the samples. Temperature-dependent EPR measurements (100–300 K) confirmed the paramagnetic nature of the oxygen vacancy signals, which followed Curie–Weiss behavior ($I \propto 1/T$) without evidence of ferromagnetic ordering. This paramagnetism is essential for catalytic applications, as it indicates isolated, non-interacting vacancy sites that can independently trap and activate molecular oxygen. Simulated EPR spectra using an $S = 1/2$ spin Hamiltonian with isotropic g -factors ($g_x = g_y = g_u = 2.003$) and Lorentzian line shapes reproduced the experimental data with excellent fidelity, further substantiating the assignment to single-electron-trapped oxygen vacancies [27].

3.7.6. Raman, FTIR, and UV-Vis Diffuse Reflectance Spectroscopy

Raman spectroscopy (Figure S2) provided complementary structural information on the carbonaceous matrix. The optimal Pt/MnO_x/C catalyst exhibited characteristic D and G bands at $\sim 1350\text{ cm}^{-1}$ and $\sim 1580\text{ cm}^{-1}$, respectively, with an ID/IG intensity ratio of 1.38, which is substantially lower than raw oil sludge (1.85) and Control-1 (1.91), but slightly higher than highly graphitized carbon. This intermediate disorder index reflects the successful conversion of amorphous petroleum-derived carbon into partially ordered graphitic domains [28] during pyrolysis, while retaining sufficient structural defects (edge sites, heteroatom dopants) to anchor Pt nanoparticles and facilitate charge transfer. The emergence of a sharp 2D band at 2695 cm^{-1} (FWHM = 38 cm^{-1}) with Lorentzian deconvolution into two sub-bands (2695 and 2720 cm^{-1}) confirmed the presence

of 3–5 layer graphene domains derived from blueberry extract polyphenol carbonization. The Mn–O stretching vibrations at 640 cm^{-1} (MnO) and 655 cm^{-1} (Mn_3O_4) exhibited an intensity ratio $I_{640}/I_{655} = 2.1$, consistent with the predominance of MnO over Mn_3O_4 in the near-surface region probed by Raman spectroscopy. FTIR spectroscopy (Figure S3) tracked the chemical evolution from raw blueberry extract to the final calcined catalyst. The fresh extract displayed characteristic O–H stretching (3400 cm^{-1}), C=O stretching (1700 cm^{-1}), aromatic C=C (1600 cm^{-1}), and anthocyanin fingerprint bands ($700\text{--}900\text{ cm}^{-1}$). Upon complexation with H_2PtCl_6 , the C=O intensity diminished, and a new Pt–O–C vibrational mode appeared at 580 cm^{-1} , confirming metal–phenolate coordination. After calcination at $750\text{ }^\circ\text{C}$, all organic signatures were eliminated, leaving only metal–oxygen vibrations: Mn–O stretches at 580 cm^{-1} and 470 cm^{-1} , and a Pt–O–Mn bridge vibration at 420 cm^{-1} . The latter is mechanistically significant, as it evidences direct metal–support interaction between Pt and the MnO_x matrix [21–24], which is absent in Control-2 (no polyphenol-mediated interface engineering). UV-visible diffuse reflectance spectroscopy (UV-vis DRS, Figure S4) revealed the optical properties of the catalysts and their relevance to VUV photocatalysis. The optimal Pt/ MnO_x /C exhibited enhanced absorption in the 200–400 nm region relative to Control-1 and raw EMR, attributed to Pt d–d interband transitions and a surface plasmon resonance shoulder at $\sim 420\text{ nm}$ characteristic of ultrafine Pt nanoparticles ($<3\text{ nm}$). Both MnO (3.18 eV) and Mn_3O_4 (2.35 eV) are strongly absorbing at 185 nm (6.7 eV), with absorption coefficients $\alpha > 10^5\text{ cm}^{-1}$. Consequently, VUV photons are absorbed within the first 10–20 nm of the oxide surface. However, the hierarchical micro-mesoporous architecture ($S_{\text{met}} = 238\text{ m}^2\text{ g}^{-1}$) ensures that the majority of catalyst particles are within this penetration depth, and photon scattering at pore walls distributes the excitation throughout the porous bed. The critical advantage of 185 nm radiation is not bulk penetration but the generation of gas-phase ROS ($\text{O}(^3\text{P})$, $\text{OH}\bullet$) that migrate into mesopores and react at active sites.

3.8. Catalytic Performance and Kinetics

3.8.1. CO Oxidation Efficiency and Reaction Kinetics

The VUV-driven photocatalytic CO oxidation performance of the optimal Pt/ MnO_x /C catalyst and reference materials is summarized in Figure 9a and Table 5. Under standardized conditions ($25\text{ }^\circ\text{C}$, 101.3 kPa, $\text{CO}:\text{air} = 1:10,000\text{ (v/v)}$, and 185 nm VUV irradiation $\approx 5.2\text{ mW cm}^{-2}$), the optimal catalyst achieved a CO oxidation efficiency of $97.79 \pm 0.10\%$ after 30 min, with a pseudo-first-order rate constant $k_{\text{obs}} = 0.128\text{ min}^{-1}$. The optimal Pt/ MnO_x /C catalyst achieved a CO oxidation efficiency of $97.79 \pm 0.10\%$ after 30 min, compared with 46.58%, 44.36%, and 58.2% for Control-1, Control-2, and commercial Pt/ Al_2O_3 , respectively. The corresponding endpoint-based apparent rate constants, calculated from these conversions as $k_{\text{obs}} = -\ln(1 - \eta)/t$, were 0.128, 0.020, 0.019, and 0.029 min^{-1} , respectively; these single-point constants are used strictly for comparative benchmarking under identical conditions. The optimal catalyst therefore achieved higher 30 min CO conversion than the commercial reference while containing less than half its platinum loading (1.12 wt% versus 2.5 wt%). Under dark conditions, all catalysts exhibited negligible CO conversion ($<5\%$), and blank reactor experiments confirmed $<2\%$ non-catalytic CO removal via photolysis or adsorption, establishing that the observed activity is predominantly photocatalytic in origin. The superior activity of the optimal catalyst can be rationalized through the synergistic interplay of three structural features: (i) ultrafine Pt0 nanoparticles (2.1 nm) with high metallic surface area and optimal CO adsorption energetics; (ii) abundant oxygen vacancies (28.3% of total surface oxygen) that serve as trapping and dissociation sites for VUV-generated reactive oxygen species; and (iii) N-doped carbon domains that enhance electron transfer from the MnO_x support to Pt

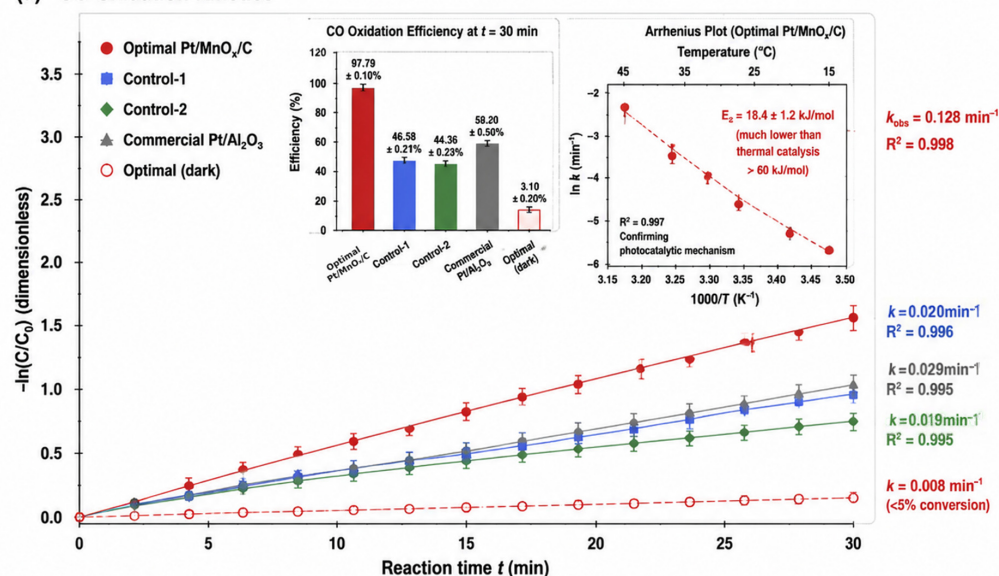
nanoparticles, thereby suppressing charge recombination. The turnover frequency (TOF), calculated as the number of CO molecules converted per surface Pt atom per second, was $2.5 \times 10^{-4} \text{ s}^{-1}$ at 25 °C based on CO chemisorption data (Table S4), and the corresponding Pt-mass-normalized initial activity was $5.5 \times 10^{-3} \text{ mol}_{\text{CO}} \text{ g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ under the specified VUV irradiation conditions. This TOF value, obtained at a Pt loading of merely 1.12 wt%, is lower than the literature values for thermal Pt/MnO_x catalysts [4,21–24] because our reaction operates at ambient temperature with VUV photons supplying the activation energy rather than thermal energy; both the per-surface-Pt-atom (TOF) and per-gram-Pt normalizations are provided to enable fair comparison with the 2.5 wt% Pt commercial reference. Arrhenius analysis of the temperature dependence (15–45 °C) yielded an apparent activation energy $E_a = 18.4 \pm 1.2 \text{ kJ mol}^{-1}$ (Figure 9a), substantially lower than the $>60 \text{ kJ mol}^{-1}$ typically reported for thermal catalytic CO oxidation over Pt-based catalysts [3,4,21–24,29]. This marked reduction in activation barrier is diagnostic of a photocatalytic mechanism wherein VUV photons directly generate reactive oxygen species (O^3P , O^1D , $\text{OH}\cdot$) that bypass the rate-limiting O_2 dissociation step required in thermal catalysis. The linearity of the Arrhenius plot ($R^2 > 0.99$) over the investigated temperature range is consistent with an unchanged reaction mechanism and with the absence of severe mass-transport artifacts, in line with the transport-favorable textural properties of the bed ($D_p = 7.1 \text{ nm}$ mesoporosity, 40–60 mesh granules). The contribution of pure gas-phase photochemistry was further bounded using the existing dataset: the Pt-free carbonized MnO_x/C support converted only 12.4% of CO under identical irradiation, whereas the empty reactor (photolysis plus wall adsorption) accounted for $<2\%$ conversion. Because 185 nm photons generate $\text{O}^3\text{P}/\text{O}_3$ in the O_2 -containing feed regardless of the catalyst, the difference between 12.4% (support alone) and 97.79% (optimal catalyst) demonstrates that the reaction is dominated by Pt-catalyzed surface pathways, although a minor gas-phase contribution cannot be excluded. Finally, based on the measured irradiance (5.2 mW cm^{-2} at 185 nm, corresponding to a photon flux density of $4.8 \times 10^{15} \text{ photons cm}^{-2} \text{ s}^{-1}$) and the number of CO molecules converted (7.6×10^{16} molecules in 30 min within the 31.4 mL reactor), the apparent quantum efficiency is estimated to be of the order of 10^{-3} – 10^{-2} per unit irradiated geometric area ($\approx 0.09\%$ even under the conservative assumption of uniform irradiation of a ca. 10 cm^2 bed), confirming that the process operates in a photon-limited regime.

3.8.2. Cycling Stability and Post-Reaction Characterization

Cycling stability was evaluated over five consecutive CO oxidation runs under identical conditions, with vacuum evacuation ($<1 \times 10^{-3} \text{ Pa}$, 15 min) between cycles to remove adsorbed products and unreacted gases (Figure 9b). The optimal catalyst exhibited exceptional durability, retaining 97.02% CO oxidation efficiency in the fifth cycle (97.79% in the first cycle), corresponding to a gradual decay rate of merely 0.154% per cycle and an overall activity retention of 99.2%. This stability is remarkable for a waste-derived catalyst operating under VUV irradiation, where photon-induced sintering and oxidative degradation are common failure modes. Post-cycling characterization provided mechanistic insight into the origin of this robustness. TEM imaging of the spent catalyst revealed a minimal increase in average Pt particle size from $2.1 \pm 0.4 \text{ nm}$ to $2.3 \pm 0.5 \text{ nm}$, indicating negligible thermal or photon-induced sintering. XPS analysis confirmed the preservation of Pt oxidation states: the Pt 4f spectrum of the spent catalyst was virtually superimposable with that of the fresh sample, with no shift in binding energy or change in the $\text{Pt}^0/\text{Pt}^{2+}$ ratio. Similarly, the S 2p spectrum maintained its exclusive sulfate signature at 168.5 eV, with no emergence of sulfide or thiolate species that would indicate sulfur poisoning. Carbon balance verification by online GC-TCD consistently exceeded $98.7 \pm 1.2\%$ across all cycles, with CO_2 detected as the sole carbon-containing product, confirming the absence of carbon

deposition (coke formation) or partial oxidation byproducts (formaldehyde, formic acid) that could deactivate the catalyst through site blocking.

(a) CO Oxidation Kinetics



(b) Cycling Stability Test

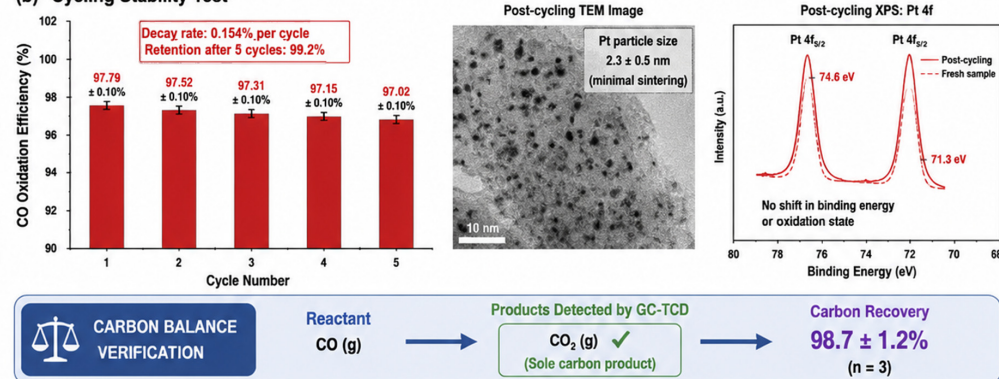


Figure 9. VUV photocatalytic CO oxidation performance and stability; (a): CO oxidation kinetics curves; (b): Cycling stability test (created with BioRender.com and Adobe Illustrator). (In the carbon-balance schematic, the arrows indicate the sequence from CO reactant to product detection and carbon-recovery assessment. The check mark denotes CO₂ as the sole carbon-containing product detected by GC – TCD).

3.8.3. Mechanistic Insights from In Situ DRIFTS

In situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) under VUV irradiation provided real-time molecular-level insight into the surface species involved in the reaction (Figure S6). Upon exposure of the optimal catalyst to the CO:air reactant mixture under 185 nm irradiation, a prominent absorption band at 2065 cm^{-1} emerged and intensified within the first 10 min, assigned to linearly adsorbed CO on Pt⁰ (Pt⁰-CO). A weaker band at 1850 cm^{-1} , attributed to bridge-bonded CO on Pt, was also detected. Simultaneously, bands at 1540 cm^{-1} (bidentate carbonate on MnO_x), 1420 cm^{-1} (monodentate carbonate), and 1220 cm^{-1} (bicarbonate) developed progressively, while a gas-phase CO₂ band at 2340 cm^{-1} intensified monotonically. The integrated intensity of the Pt⁰-CO band exhibited a clear anti-correlation with the CO₂ band ($R = -0.98$), establishing a direct kinetic link between CO adsorption on Pt and CO₂ production [21,22,24,29]. Negative bands at 3670 cm^{-1} (surface O-H stretching) and 1620 cm^{-1} (adsorbed H₂O) indicated consumption of surface hydroxyl groups during the reaction, consistent with the participation of OH· radicals

generated by VUV photolysis of residual moisture ($\text{H}_2\text{O} + h\nu \rightarrow \text{OH}\cdot + \text{H}\cdot$, $E_{\text{diss}} = 5.11 \text{ eV}$). The temporal evolution of adsorbed species supports a Langmuir–Hinshelwood mechanism [21,22,29]: (Step 1) CO adsorption on Pt^0 via back-donation from Pt 5d to CO $2\pi^*$; (Step 2) O_2 dissociative adsorption at oxygen vacancy sites (O_v) on MnO_x , facilitated by VUV-generated atomic oxygen; (Step 3) surface reaction between adsorbed CO^* and O^* species at the Pt– MnO_x interface; and (Step 4) CO_2 desorption with concurrent regeneration of the oxygen vacancy. The low apparent activation energy (18.4 kJ mol^{-1}) is consistent with the surface reaction (Step 3) being rate-determining, as both reactants are pre-adsorbed and activated, eliminating the high-energy barrier associated with gas-phase O_2 dissociation. These DRIFTS data are qualitative. Transient switching experiments and, ideally, ^{18}O isotopic labeling would be required to definitively exclude a Mars–van Krevelen contribution (CO consumption of lattice oxygen followed by vacancy re-oxidation from gas-phase O_2). The four-step Langmuir–Hinshelwood scheme is therefore presented as a working model consistent with the available data, and this limitation is explicitly acknowledged.

3.9. Catalytic Mechanism and Structure–Activity Correlations

The comprehensive structural, spectroscopic, and kinetic data presented above enable the construction of a unified mechanistic framework for VUV-driven photocatalytic CO oxidation over the Pt/ MnO_x /C catalyst (Figures 1 and 7b). Under 185 nm irradiation (photon energy of 6.7 eV), two primary photolytic pathways generate reactive oxygen species (ROS) in the gas phase and at the catalyst surface: (i) direct photodissociation of molecular oxygen ($\text{O}_2 + h\nu \rightarrow \text{O}(^3\text{P}) + \text{O}(^1\text{D})$, bond dissociation energy 5.12 eV) and (ii) photolysis of residual water vapor ($\text{H}_2\text{O} + h\nu \rightarrow \text{OH}\cdot + \text{H}\cdot$, bond dissociation energy 5.11 eV [5–7]). These ROS are subsequently trapped and activated at oxygen vacancy sites (O_v) on the MnO_x surface, where the coordinatively unsaturated $\text{Mn}^{2+}/\text{Mn}^{3+}$ centers facilitate electron transfer to adsorbed O_2 , generating superoxide (O_2^-) and atomic oxygen (O^-) intermediates. Concurrently, CO molecules adsorb on the Pt^0 nanoparticles via back-donation from filled Pt 5d states to the CO $2\pi^*$ antibonding orbital, weakening the $\text{C}\equiv\text{O}$ triple bond and polarizing the carbon atom for nucleophilic attack [3,4,21–24]. The N-doped carbon matrix plays a critical auxiliary role by mediating long-range electron transfer from the MnO_x conduction band to the Pt Fermi level, thereby maintaining charge separation and preventing electron–hole recombination [25,26]. Pyridinic and pyrrolic nitrogen species, with their localized lone-pair electrons, create electron-rich domains that attract photogenerated holes and facilitate their migration away from the active Pt– MnO_x interface. The Schottky barrier formed at the Pt– MnO_x junction (work function of Pt = 5.6 eV, MnO band gap = 3.2 eV) further promotes unidirectional electron flow from the support to the metal, enhancing the reducibility of Pt surface sites and stabilizing the Pt^0 oxidation state under reaction conditions [22,24–26]. The structure–activity correlations derived from this study are summarized as follows: (i) bacterial fermentation is indispensable for creating the hierarchical mesoporous architecture ($S_{\text{met}} = 238 \text{ m}^2 \text{ g}^{-1}$) that ensures efficient reactant diffusion and high active site accessibility; (ii) polyphenol-mediated Pt dispersion is essential for achieving ultrafine metallic Pt^0 nanoparticles (2.1 nm, 38.2% dispersion) with optimal CO adsorption energetics; (iii) the mixed-valence MnO_x matrix ($\text{Mn}^{2+}/\text{Mn}^{3+} = 1.8:1$) with abundant surface oxygen defects (28.3% of the O 1s envelope, an upper bound corroborated by EPR) provides the primary sites for O_2 activation and ROS trapping; and (iv) N-doped carbon domains (2.8 at.% N, predominantly pyridinic/pyrrolic) enhance electron transport and stabilize the heterostructure against deactivation. The absence of any one of these components (as demonstrated by Control-1 and Control-2) results in a >50% loss of catalytic activity, underscoring the genuine synergy among biological pretreatment, polyphenol chemistry, and waste-derived inorganic phases.

3.10. Sustainability and Scalability Considerations

Beyond the fundamental mechanistic insights, the present work establishes a compelling sustainability paradigm for hazardous waste valorization [30–33]. The dual utilization of EMR and oil sludge—two of the most environmentally burdensome industrial byproducts—transforms a linear “cradle-to-grave” disposal model into a circular “cradle-to-cradle” resource loop [34–37]. The overall synthetic yield, defined as the mass ratio of final catalyst to initial EMR + oil sludge mixture, was 25–35 wt%, which is competitive with conventional synthetic catalyst preparation routes that typically exhibit yields of 30–50 wt% but require expensive virgin precursors and energy-intensive solvent-based protocols. The biological pretreatment step operates at ambient pressure and moderate temperature (35 °C) [38,39], consuming only microbial nutrients (lactate, yeast extract) that are substantially cheaper than synthetic surfactants or template agents used in conventional mesoporous material synthesis. The polyphenol-mediated Pt reduction strategy eliminates the need for hazardous chemical reductants such as NaBH₄ or hydrazine [40,41], and the blueberry extract—a food-grade agricultural byproduct—contributes nitrogen doping without requiring additional NH₃ or urea post-treatments. The calcination protocol (750 °C, 6 h, and heating rate of 2 °C min^{−1}) is milder than conventional Pt catalyst preparation (often >800 °C with H₂ reduction), and the slow heating rate prevents Pt sintering without requiring complex atmosphere control. From a life-cycle perspective, the carbon footprint of the present catalyst is anticipated to be substantially lower than that of commercial Pt/Al₂O₃, given that (i) the support and active phase precursors are waste-derived rather than mined or synthesized *de novo*, (ii) the Pt loading is reduced by >50% while maintaining superior activity, and (iii) the ambient-temperature VUV operation eliminates the energy penalty associated with thermal catalysis (150–400 °C). Future techno-economic analysis and life-cycle assessment will be necessary to quantify these sustainability benefits and guide industrial scale-up, particularly regarding the logistics of waste feedstock collection, microbial consortium maintenance, and continuous-flow reactor design for practical air purification applications [42]. Finally, because both feedstocks contain heavy metals (Pb, Hg, Cr, and Cd) and sulfur, the environmental safety of the derived catalyst hinges on the immobilization of these elements. The structural evidence presented here—crystalline CaSO₄ retention (22.4 wt%, Rietveld), the exclusive sulfate S 2p signature before and after reaction, and encapsulation of residual ash within the carbon-MnO_x matrix—indicates effective stabilization during the 750 °C calcination. Nevertheless, standard leaching tests (e.g., HJ/T 299 or EPA TCLP) on the fresh and spent catalysts, together with post-reaction ICP analysis of Pt retention and long-term continuous-flow operation under realistic relative humidity and higher CO levels, are indispensable before the material can be presented as a safe and circular solution.

4. Conclusions

This study presents a closed-loop, sustainable strategy for fabricating high-performance Pt/MnO_x/C composite catalysts from electrolytic manganese residue and oil sludge via anaerobic co-fermentation with mixed halophilic desulfurizing bacteria and polyphenol-mediated Pt dispersion using blueberry extract. The optimal catalyst (1.12 wt% Pt) achieves a vacuum ultraviolet photocatalytic CO oxidation efficiency of 97.79% at ambient temperature with an endpoint-derived apparent rate constant of 0.128 min^{−1}, representing 6.4-fold and 4.4-fold improvements in apparent rate constant over biologically untreated controls and commercial Pt/Al₂O₃, respectively. Bacterial pretreatment decomposes petroleum hydrocarbons and templates hierarchically porous MnO_x/C supports (238 m² g^{−1}), while blueberry polyphenols reduce and stabilize ultrafine Pt⁰ nanoparticles (2.1 ± 0.4 nm, 38.2% dispersion). Proteins and amino acids present in the crude extract provide the nitrogen

source for the formation of nitrogen-doped carbon domains (2.8 at.% N), which modulate interfacial electron transfer. Structural synergy among Pt⁰, a mixed-valence MnO_x matrix (Mn²⁺/Mn³⁺ = 1.8:1) with abundant surface oxygen defects, and N-doped carbon is consistent with a Langmuir–Hinshelwood-type mechanism with an apparent activation energy of 18.4 kJ mol^{−1}. The catalyst retains 97.02% of its initial efficiency after five cycles (99.2% activity retention) with negligible Pt sintering and retention of the sulfate sulfur signature. Long-term continuous-flow operation, realistic-humidity and high-CO testing, heavy-metal leaching assessment of the fresh and spent catalyst, and post-reaction Pt quantification are identified as essential next steps. Subject to these validations, this work establishes a scientifically rigorous and technologically viable waste-to-catalyst paradigm for low-temperature air purification.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su182010261/s1>; Table S1: Detailed chemical composition of raw materials; Table S2: Characterization of blueberry extract (*Vaccinium corymbosum*, Shanxi Chengzhi Biotechnology Co.); Table S3: Textural properties of all prepared samples; Table S4: ICP-AES quantification of platinum loading and CO chemisorption data; Table S5: Screening of halophilic bacterial strains; Table S6: Detailed Micro-GC and GC-MS Operating Conditions; Table S7: FTIR Band Assignments with Literature References [43–45]; Table S8: XPS Pt 4f Peak Fitting Results and Oxidation State Ratios; Figure S1: GC-MS Analysis of fermentation products (supporting information); Figure S2: Raman spectroscopy; Figure S3: FTIR spectroscopy; Figure S4: UV-vis diffuse reflectance spectroscopy; Figure S5: EPR spectroscopy of oxygen vacancies; Figure S6: In-situ DRIFTS and carbon balance; Figure S7: TGA-DSC Analysis of Carbonized MnO_x/C in Static Air. Figure S8: EPR Signal Intensity vs. CO Oxidation Efficiency—Complete Dataset; S12: Supplementary Experimental Details; S13: Supplementary Discussion on Thermodynamic Feasibility of MnC Formation.

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