

Elemental Changes of Wahau Low-Rank Coal after Hydrogen Peroxide Pretreatment: Implications for Coal Bioavailability

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Abstract

Low-rank coal contains abundant oxygen-bearing and aliphatic structures that can be chemically modified under mild oxidative conditions. However, the significance of small elemental shifts for subsequent biological utilization remains insufficiently constrained. This study evaluates elemental changes in Wahau low-rank coal after mild hydrogen peroxide (H₂O₂) pretreatment while keeping particle size uniform. A 100-mesh coal fraction was evaluated in three states: raw coal, ultrapure-water control, and coal treated with 0.3% H₂O₂. Carbon, hydrogen, and oxygen contents were interpreted together with atomic H/C and O/C ratios. Compared to the water control (O/C=0.200, H/C=0.941; raw coal: O/C=0.203, H/C=1.108), H₂O₂ treatment increased O/C to 0.222 while leaving H/C virtually unchanged at 0.944. The shift is consistent with mild oxygenation or oxidative modification of the coal matrix rather than a simple change in carbon abundance. Comparison with published H₂O₂ studies on lignite, sub-bituminous, bituminous, and anthracitic coals indicate that oxygenation commonly accompanies structural modification. However, the extent and biological consequences depend strongly on coal rank and treatment severity. These elemental shifts indicate increased matrix polarity and potential microbial accessibility rather than direct bioconversion.

Keywords: Low-Rank Coal, Lignite, Hydrogen Peroxide, Elemental Analysis, H/C ratio, O/C ratio

INTRODUCTION

Coal rank strongly influences chemical reactivity, as increasing coalification generally increases aromatic condensation and decreases oxygen content, H/C, and the abundance of easily cleaved functional groups. High oxygen content and abundant reactive structures make low-rank coals well-suited for mild chemical conversion rather than conventional combustion. Oxidative pretreatment leverages these features by cleaving weak bridge bonds to yield more polar, low-molecular-weight products under mild conditions (Mae et al., 2001; Yu et al., 2014).

Hydrogen peroxide (H₂O₂) is attractive for coal pretreatment because it is a strong oxidant that can operate under comparatively mild conditions and ultimately decomposes to water and oxygen. Earlier work on sub-bituminous coal demonstrated substantial mineral and sulfur removal with H₂O₂, while studies on lignite have shown oxidation of aromatic structures, cleavage of bridge linkages, and formation of carboxylic acids and other water-soluble products (Mukherjee et al., 2001; Duskocil et al., 2014; Liu et al., 2015). This oxidative response is rank-dependent, with low-rank coals exhibiting higher reactivity than higher-rank coals (Chen et al., 2018).

For microbially enhanced coalbed methane and related biological conversion routes, the key issue is whether oxidation produces a matrix or soluble fraction accessible to microorganisms. Partial oxidation and H₂O₂ pretreatment have been associated with increased methanogenic potential, short-chain carboxylic acids, soluble organics, and biomethane in several low-rank coal systems (Jones et al., 2013; Haq et al., 2018; Liu et al., 2019; Zhang et al., 2023). However, elemental composition alone cannot demonstrate bioavailability and provides only a first-order indication of

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chemical changes through atomic H/C and O/C ratios. Increased oxygenation does not necessarily imply greater microbial accessibility or conversion, as oxidative treatment may promote selective dissolution or generate compounds with different biodegradability. Moreover, the relationship between elemental changes in the residual coal matrix and actual biological utilization remains insufficiently established for Indonesian low-rank lignite. Therefore, controlled evaluation of elemental and atomic-ratio changes, with appropriate water control, provides a preliminary basis for distinguishing the chemical effects of mild H₂O₂ treatment from changes associated with water exposure and subsequent sample handling.

The Muara Wahau deposit in East Kalimantan is an important Indonesian low-rank coal resource whose high oxygen functionality favors oxidative pretreatment. Recent studies on Indonesian low-rank coals further confirm that H₂O₂ treatment alters both inorganic and organic coal fractions, affecting fuel quality, elemental distribution, and matrix reactivity (Ishaq et al., 2026; Jamastuti et al., 2026; Ardian et al., 2026). Building on this context, the present study evaluates the elemental response of Muara Wahau lignite to mild H₂O₂ pretreatment. Particular attention is given to changes in C, H, and O contents and atomic H/C and O/C ratios as indicators of oxidative modification, and to their potential implications for coal bioavailability.

LITERATURE REVIEW

Hydrogen peroxide oxidation and coal rank effects

Mild H₂O₂ oxidation preferentially cleaves weak bridge linkages and aliphatic side chains while largely preserving the aromatic framework (Mae et al., 2001; Xiong et al., 2020). In low-rank coals, this oxidative degradation converts insoluble organic matter into water-soluble polycarboxylic acids and oxygenated functional groups, with spectroscopic evidence of side-chain and bridge-bond destruction while much of the aromatic ring framework remained intact during the milder stages (Doskocil et al. 2014; Liu et al. 2015; Xiong et al. 2020). H₂O₂ oxidation was also reported to remove inorganic/sulfur phases, shifting solid-phase elemental percentages (Mukherjee et al., 2001; Doskočil et al., 2014; Liu et al., 2015; Ishaq et al., 2026). Consequently, changes in solid-phase elemental percentages may reflect relative compositional shifts caused by dissolution or mineral removal rather than proportional changes in the absolute mass of C, H, or O.

Elemental ratios and bioavailability as interpretive proxies

Atomic H/C and O/C ratios provide compact indicators of relative hydrogenation and oxygenation. Increasing O/C generally reflects greater oxygen-containing functionality, whereas H/C changes may indicate modification of aliphatic structures, dehydrogenation, aromatization, or selective removal of hydrogen-rich fractions. Studies using FTIR, NMR, and GC-MS have confirmed increased oxygen-containing groups following H₂O₂ treatment (Haq et al., 2018; Yan et al., 2021; Zhang et al., 2023). However, greater solubility and oxygenation do not necessarily indicate complete microbial utilization, as oxidation can produce both labile and recalcitrant dissolved organics (Liu et al., 2019).

Across low-rank coal systems, partial or assisted oxidation has been associated with increased methanogenic potential, biomethane production, and organic-matter dissolution (Jones et al., 2013; Chen et al., 2018; Zhang et al., 2023; Song et al., 2023). These findings support the use of elemental oxygenation as a chemical proxy for potential microbial accessibility, while maintaining the distinction between indirect chemical indicators and direct evidence of biological

utilization.

RESEARCH METHODOLOGY

Materials

The coal sample used in this study was lignite collected from the Muara Wahau area of the Kutai Basin, East Kalimantan, Indonesia. The Wahau deposit is a large low-rank lignite resource in Indonesia (Ardian et al., 2026). To maintain a narrowly defined experimental scope, this study used only the 100-mesh particle fraction and did not evaluate particle-size effects.

The main reagent used for oxidative pretreatment was H_2O_2 , while ultrapure water was used for the control treatment. Coal preparation involved crushing and milling for size reduction, followed by sieving through a 100-mesh sieve to obtain a relatively uniform particle fraction.

Batch Hydrogen Peroxide Pretreatment

Oxidative pretreatment was conducted in a laboratory-scale batch system using 20 g of 100-mesh lignite and 200 mL of treatment solution, corresponding to a nominal solid-to-liquid ratio of 1:10 (g:mL). The treatment solution contained 0.3% H_2O_2 . The lignite- H_2O_2 mixtures were maintained for 20 days at room temperature (approximately 25°C). The pretreatment experiment was conducted in triplicate to improve experimental consistency. In parallel, an ultrapure-water control distinguished changes associated with H_2O_2 exposure from those potentially resulting from prolonged coal-water interaction. For the control, ultrapure water replaced H_2O_2 under otherwise comparable treatment conditions. Following pretreatment, the batch system yielded two operational fractions: a liquid fraction containing soluble reaction products and a residual solid lignite fraction. Only the solid residue was considered in the present elemental-composition assessment.

Elemental Analysis and Atomic Ratios

Ultimate characterization was performed to determine the elemental compositions of C, H, N, and O for the untreated lignite, the ultrapure-water control, and lignite after H_2O_2 pretreatment. This study focuses primarily on C, H, and O because these elements most directly indicate changes in the organic matrix associated with oxidative treatment. Particular emphasis was placed on H/C and O/C ratios, which provide a normalized basis for examining relative changes in hydrogenation and oxygenation of the coal matrix. Atomic ratios were calculated from elemental mass percentages using the following equations: Atomic H/C and O/C ratios were calculated from mass percentages using standard atomic weights as follows:

$$\begin{aligned} H/C &= (H/1.008)/(C/12.011) \\ O/C &= (O/15.999)/(C/12.011) \end{aligned}$$

where C, H, and O represent the respective elemental contents in wt.%.

FINDINGS AND DISCUSSION

Elemental composition of raw, water-control, and mildly oxidized coal

The elemental results are summarized in Table 1. Raw Wahau coal contained 57.22% C, 5.32% H, and 15.46% O. After exposure to ultrapure water, C and O were 61.31% and 16.37%, respectively, while H decreased to 4.84%. Mild H_2O_2 treatment produced 59.21% C, 4.69% H, and 17.52% O. Relative to the water control, the H_2O_2 -treated coal contained 7.0% more oxygen on a relative basis, while C and H percentages were modestly lower. Relative to raw coal, oxygen was 13.3% higher after H_2O_2 treatment.

Table 1. Elemental composition and atomic ratios of Wahau coal

Conditions	C	H	O	H/C	O/C
	wt% (db)			atomic ratio	
Raw coal	57.22	5.32	15.46	1.108	0.203
Ultrapure-water control	61.31	4.84	16.37	0.941	0.200
H ₂ O ₂	59.21	4.69	17.52	0.944	0.222

The direction of the oxygen change is the most robust feature of this limited dataset. However, the C content demonstrates why isolated percentages require caution. Carbon is higher in both the water control and the H₂O₂ treatment than in raw coal, which does not imply carbon production. Instead, coal treatment can remove or redistribute moisture, mineral matter, heteroatoms, and soluble organic fractions, thereby changing the denominator of the ultimate-analysis composition. [Jamastuti et al. \(2026\)](#) independently showed that H₂O₂ pretreatment redistributes major and trace elements between solid and aqueous phases, while [Ardian et al. \(2026\)](#) documented changes in Wahau coal properties under stronger 3% H₂O₂ treatment. Therefore, the present data are interpreted primarily through H/C and O/C ratios, not through C content alone.

Atomic H/C-O/C shift and Van Krevelen interpretation

The raw coal had H/C=1.108 and O/C=0.203. The water control shifted to H/C=0.941 and O/C=0.200, indicating that water exposure and subsequent sample handling alone produced a substantial change in the measured H/C ratio relative to raw coal. This makes the water control essential for isolating the incremental effect of H₂O₂. Relative to that control, mild H₂O₂ treatment increased O/C from 0.200 to 0.222, an increase of approximately 11%, while H/C changed from 0.941 to 0.944. Thus, the clearest H₂O₂-specific signal is increased oxygenation with almost no additional change in hydrogen-to-carbon ratio.

Figure 1 shows that while comparing raw and H₂O₂-treated coal suggests coupled O/C and H/C shifts, the water control confirms that the H/C decrease occurred independently of oxidation. The incremental H₂O₂ effect is better described as mild oxygenation or oxidative functionalization than as generalized dehydrogenation. This interpretation is consistent with international studies reporting formation or enrichment of oxygen-containing groups after H₂O₂ treatment, but the present dataset does not identify which specific groups increased.

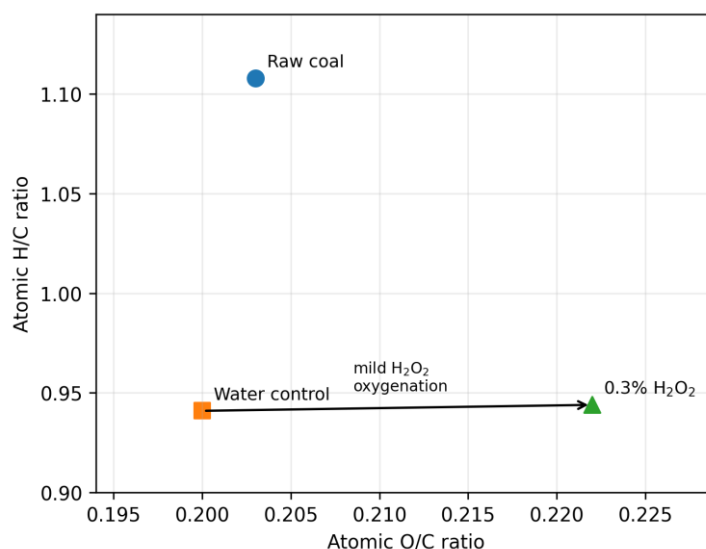


Figure 1. Van Krevelen-style representation of raw Wahau coal, ultrapure-water control, and 0.3% H₂O₂ treatment

Comparison with H₂O₂-treated coals of different ranks

Table 2 places the Wahau result in the context of selected international H₂O₂ studies. The literature consistently shows that H₂O₂ can introduce or expose oxygenated structures, cleave weak linkages, and generate water-soluble products, but the magnitude and consequences vary with coal rank. Lignite and sub-bituminous coals generally provide the clearest evidence of extensive depolymerization or solubilization under mild-to-moderate conditions. In contrast, higher-rank coals may require stronger treatment and show less improvement in bioavailability.

Table 2. Relevant studies on H₂O₂-induced elemental/structural modification across coal ranks

Study	Coal rank reported	H ₂ O ₂ treatment	Evidence type	Main relevance to Wahau
Doskočil et al. (2014)	Lignite	H ₂ O ₂ oxidation; 30-60°C	Direct products / molecular characterization	Oxidation of aromatic structures; hydrophilic fraction rich in low-MW carboxylic acids.
Haq et al. (2018)		H ₂ O ₂ pretreatment	Direct solubility/organic-acid data plus chemical characterization	Enhanced lignite solubility and organic acids; supports potential microbial accessibility.
Chen et al. (2018)	Sub-bituminous and medium-volatile bituminous	Multiple H ₂ O ₂ doses, 1-30 d, UV-assisted	Direct soluble organics, GC-MS, methane bioassay	Strong response in sub-bituminous coal; weak response in higher-rank bituminous coal.

Study	Coal rank reported	H ₂ O ₂ treatment	Evidence type	Main relevance to Wahau
Liu et al. (2019)	Sub-bituminous	3% H ₂ O ₂ ; extended treatment	Direct TOC/organic compounds and methane assay	Generated labile short-chain acids plus recalcitrant organics; oxygenation does not imply complete biodegradability.
Xiong et al. (2020)	Low rank	H ₂ O ₂ at 60°C (10 hr)	FTIR, 13C NMR, product analysis	Cleavage of side chains/bridge bonds and extensive conversion under controlled oxidation.
Guo et al. (2021)	Anthracite	30% H ₂ O ₂ (12 hr) under reported optimum	FTIR and methane assay	Even anthracite can be functionalized, but stronger treatment was used.
Zhang et al. (2023)	Lignite	H ₂ O ₂ pretreatment of huminite-enriched fractions	Ultimate analysis, FTIR, biomethane assay	Oxygenated functional groups and huminite reactivity linked to greater dissolution and methane production.
Wei et al. (2024)		Optimized H ₂ O ₂ pretreatment	Physicochemical analyses and biogas assay	Shows treatment severity matters; prolonged oxidation can reduce readily bioavailable organic matter.

Rank-coal variation showed that lower-rank coals were more reactive to H₂O₂ due to lower structural condensation, though treatment severity can overcome rank resistance in higher-rank coals ([Chen et al., 2018](#); [Xie et al., 2019](#); [Guo et al., 2021](#); [Zhao et al., 2023](#)). The Wahau response is less intense than those reported in studies using concentrated H₂O₂, elevated temperatures, UV activation, or long contact times. That difference is expected because the treatment uses 0.3% H₂O₂. Therefore, the increase in O/C from 0.200 in the water control to 0.222 after treatment is interpreted as an early or mild oxidative response rather than deep depolymerization. In this respect, the Wahau result is directionally consistent with low-rank coal literature without reproducing the severe solubilization conditions used in some previous studies.

Implications for potential coal bioavailability

From a biological perspective, increased O/C may enhance coal polarity, hydrophilicity, and coal–water interactions, improving microbial accessibility ([Haq et al., 2018](#); [Chen et al., 2018](#); [Zhang et al., 2023](#); [Song et al., 2023](#)). However, the response to H₂O₂ concentration may not be linear. Previous work showed that increasing H₂O₂ initially improved desulfurization and deashing, whereas further increases beyond an optimum concentration resulted in a decline, attributed to

recombination of excess hydroxyl radicals and reduced oxidation (Zuo et al., 2026). Thus, treatment severity requires optimization. Because the present study evaluated 0.3% H_2O_2 , the optimum concentration for enhancing accessibility while minimizing excessive oxidation or carbon loss cannot be established.

The interpretation of increased O/C is also limited by the characterization scope. Only the residual solid fraction was analyzed, while the dissolved fraction generated during H_2O_2 treatment was not characterized. Therefore, the O/C increase cannot distinguish oxygenation of the residual coal matrix from selective dissolution or redistribution of organic and inorganic components. Moreover, the absence of direct measurements of dissolved organic carbon, soluble organic compounds, microbial utilization, and methane production means that increased O/C should be regarded as evidence of chemical oxygenation and a potential indicator of accessibility, rather than evidence of enhanced biodegradability or biomethane production.

FTIR, XPS, NMR, SEM, and BET analyses, together with dissolved organic carbon, soluble-product, and microbial methanogenesis assessments, would help clarify the structural, surface, and biological consequences of pretreatment. This is important because excessive oxidation may generate recalcitrant compounds or deplete labile carbon (Liu et al., 2019; Wei et al., 2024). For Wahau coal, the H_2O_2 treatment provides an indication of oxygenation, with O/C increasing while H/C remained essentially unchanged relative to the water control, but further optimization and biological validation are required.

CONCLUSION AND FURTHER RESEARCH

Mild 0.3% H_2O_2 pretreatment of 100-mesh Wahau low-rank coal primarily induces incremental oxygenation of the coal matrix. Oxygen content increased from 16.37% in the water control to 17.52% after treatment, while atomic O/C increased from 0.200 to 0.222. An ultrapure-water control is essential, as it shows that the reduction in H/C relative to raw coal occurs independently of oxidant exposure, whereas H_2O_2 specifically increases the atomic O/C without altering the H/C baseline. This shift confirms mild oxidative functionalization rather than extensive structural dehydrogenation or deep depolymerization.

These elemental shifts align with oxidative patterns reported in low-rank coal literature, where H_2O_2 commonly increases oxygen-containing functionality and can promote depolymerization, solubilization, and biological conversion. To verify biological accessibility, future research should integrate elemental analysis with spectroscopic profiling (FTIR/XPS), dissolved organic carbon characterization, mass-balance tracking, and microbial methanogenesis assays. The broader effects of particle size, H_2O_2 concentration, oxidative solubilization, and carbon mobilization are intentionally outside the scope of this proceedings paper.

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