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Enhanced treatment of recalcitrant landfill leachate via CFA/FE-catalyzed Fenton process and subsequent activated sludge adaptation

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ABSTRACT

Landfill leachate contains significant levels of organic and inorganic substances as well as pathogens. The high concentration of chemical oxygen demand (COD) and low biochemical oxygen demand-to-chemical oxygen demand (BOD/COD) ratio indicate the leachate is poorly biodegradable and consist of substantial recalcitrant organic matter, making it difficult to treat by conventional biological wastewater treatment processes. The Fenton reaction is an advanced oxidation process that is based on the reaction between iron ions and hydrogen peroxide, generating hydroxyl radicals. This study utilises coal fly ash modified by the iron precipitation method as a Fenton catalyst. Catalyst characterization using scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), x-ray diffraction (XRD), and the acid digestion method confirmed the presence of a substantial iron content in the form of magnetite. Batch Fenton experiments showed that decolourisation of leachate was affected by pH solution, the dosage of iron catalyst, and H_2O_2. Under the following operating conditions: 2 g L^{-1} CFA/Fe, 4800 mg L^{-1} H_2O_2, pH 3, colour and dissolved organic carbon (DOC) removal reached up to 81.46% and 42.98%, respectively. Furthermore, the subsequent biological activated sludge treatment after Fenton oxidation showed that the activated sludge process could adapt to residual Fenton's reagents.

Keywords: activated sludge, heterogeneous Fenton, hybrid wastewater treatment, landfill leachate.

Tratamento aperfeiçoado de lixiviado recalcitrante de aterro sanitário via processo Fenton catalisado por CFA/FE e subsequente adaptação de lodo ativado

RESUMO

O lixiviado de aterro contém níveis significativos de substâncias orgânicas e inorgânicas, bem como de agentes patogénicos. A elevada DQO e a baixa relação DBO/DQO do lixiviado indicam que este não é biodegradável e, frequentemente, é difícil de tratar por processos convencionais de tratamento biológico de efluentes. A reação de Fenton é um processo de

oxidação avançada baseado na reação entre iões de ferro e peróxido de hidrogénio, gerando radicais hidroxilo. Este estudo utiliza cinzas volantes de carvão modificadas pelo método de precipitação de ferro como catalisador de Fenton. A caracterização do catalisador por MEV-EDS, DRX e pelo método de digestão ácida confirmou um teor apreciável de ferro sob a forma de magnetite. As experiências de Fenton em batelada mostraram que a descoloração do lixiviado foi afetada pelo pH da solução, pela dosagem do catalisador de ferro e pelo H_2O_2. Nas seguintes condições de operação: 2 g L^{-1} de CFA/Fe, 4800 mg L^{-1} de H_2O_2, pH 3, a remoção de cor e de carbono orgânico dissolvido (COD) atingiu até 81,46% e 42,98%, respetivamente. Além disso, o tratamento subsequente de lamas activadas biológicas após a oxidação de Fenton mostrou que o processo de lamas activadas pode adaptar-se aos reagentes residuais de Fenton.

Palavras-chave: Fenton heterogêneo, híbrido, lixiviado de aterro sanitário, lodos ativados, tratamento de águas residuárias.

1. INTRODUCTION

The quality and quantity of leachate vary depending on the climate, amount of precipitation, waste composition and characteristics, landfill age, and operation. The vast amount of waste that enters landfills has the potential to generate a large amount of leachate. Leachate has a high concentration of chemical and inorganic substances, as well as harmful microbes. In general, as written by Kjeldsen *et al.* (2002) and Purwanta and Susanto (2017), the characteristics of leachate have a high chemical oxygen demand (COD) value exceeding 10,000 mg L^{-1} and a low five-day biochemical oxygen demand-to-chemical oxygen demand (BOD_5/COD) ratio of <0.4 making leachate typically non-biodegradable. As a result, if leachate is not handled effectively, leachate infiltration into the soil may contaminate not only the soil but also pollute groundwater and water (Laskar *et al.*, 2022; Trihadiningrum *et al.*, 2023)

Advanced oxidation processes (AOPs) are alternative methods for treating non-biodegradable wastewater such as leachate. The Fenton process is an advanced oxidation method that generates hydroxyl radical species by reacting hydrogen peroxide (H_2O_2) with ferrous ions (Fe^{2+}) as a catalyst. Deng and Zhao (2015) stated that hydroxyl radicals are non-selective and destructive species and can oxidise complex molecules in leachate; hence they play a role in rapidly oxidising and degrading numerous organic and inorganic chemicals (Deng and Zhao, 2015).

The Fenton reaction has some distinct advantages in wastewater treatment, such as ease of application and rapid reaction time. However, the Fenton method typically has high operation costs if employed on a large-scale installation due to the use of expensive reagents such as hydrogen peroxide, the separation of soluble iron after reaction and iron sludge management as conducted by Xu (Xu *et al.*, 2021). To cope with this problem, the utilisation of iron catalysts in solid form (heterogeneous process) and waste-derived catalysts combining the Fenton reaction and biological process in hybrid treatment appears to be an attractive solution to obtain both overall treatment efficiency and potential energy savings (Tee *et al.*, 2016; Raj *et al.*, 2024)

Recent advances have highlighted the effectiveness of sequential advanced oxidation processes for landfill leachate treatment. Hosseinikhah *et al.* (2025) demonstrated that a multi-stage EC/PM–PMS/UV–EP system achieved nearly complete COD, TOC, and ammonia removal while improving biodegradability (BOD_5/COD = 0.55). Similarly, Feizi *et al.* (2026) reported that a two-stage process combining photo-electrochemical PMS activation with percarbonate/ozone/MnO_2@carbon attained COD, TOC, and ammonia removals above 90% and enhanced biodegradability to 0.62. These findings underscore the promise of staged AOPs in detoxifying complex leachates. In contrast, our study advances a circular-economy approach by reutilizing coal fly ash as a heterogeneous Fenton catalyst and directly assessing biological

adaptation following oxidation, thereby offering a simpler two-stage configuration that integrates waste-derived catalysts with typical biological treatment used in existing leachate treatment.

The use of waste as a heterogeneous Fenton catalyst is one inventive way to address the circular economy concept. In addition to being economically profitable, waste-derived materials are also environment-friendly by reducing the use of new materials thus limiting the extraction of raw materials. Previous studies showed the potential use of some waste materials as heterogeneous Fenton catalysts, such as iron ore tailings from the steel industry, fly ash, rebar flake waste from building construction, and iron sludge from the full-scale Fenton process (Adityosulindro *et al.*, 2022; Ali *et al.*, 2013; Dao *et al.*, 2017; Ye *et al.*, 2022).

According to Karanac *et al.* (2018), The Coal Steam Power Plant continuously produces a variety of solid combustion by-products, including fly ash and bottom ash, of which fly ash accounts for 65-95% of total ash. With less than 30% of total ash produced as fly ash being utilised, fly ash has become one of the most common industrial wastes produced around the world. Coal fly ash is composed of silt-sized particles with diameter size typically ranging less than 10 mm that are aggregated into spherical particles measuring 0.01-100 micrometres that are hollow spheres (cenospheres) filled with smaller amorphous particles or crystals (pelospheres). Fly ash disposal is still limited to landfilling. However, with the small size of fly ash particles, this could potentially affect the environment and human health. The main composition, such as silica, alumina, iron oxide, calcium oxide, magnesium oxide, and carbon in fly ash, might be transported into water bodies or dispersed as respirable particulates, elevating risks of aquatic contamination and respiratory exposure (Gopinathan *et al.*, 2022). For decades, fly ash was mainly utilized in adsorption processes in wastewater treatment, but in recent decades newer treatment methods such as photo-catalysis, the Fenton process, and membrane filtering have gained much attention.

The Fenton process is highlighted in this study due to its operational practicality and its proven effectiveness in degrading substantial contaminants contained in the landfill leachate. This study introduces a circular-economy–based approach by reutilizing and modifying waste materials of coal fly ash as heterogeneous Fenton catalysts, advancing beyond previous works by Niveditha and Gandhimathi (2020) and Hussain *et al.* (2021) who demonstrated the feasibility of waste-derived catalysts for landfill leachate treatment. While previous studies have shown the benefits of Fenton oxidation, its combination with biological treatment remains unclear, especially when used as a pre-treatment. Previous study by Lopez *et al.* (2004) provided only indirect evidence based on biodegradability ratios (BOD_5/COD), without examining actual biological performance.

In this study, a simulated activated sludge (AS) system is employed to directly assess the capability of the biological system to further treat Fenton-pre-treated leachate, thereby filling an important gap in understanding hybrid Fenton–biological systems. Effects of several operating parameters, such as dose of catalyst, oxidant, and pH on organic removal were further evaluated in this study.

2. MATERIAL AND METHODS

2.1. Materials

Coal fly ash (CFA) was taken from the Coal Steam Power Plant located in Muara Enim, South Sumatra, Indonesia. The CFA was filtered through 200 mesh and stored in a tightly sealed container. Leachate and AS samples were taken from the inlet of the leachate treatment plant of Bantargebang Landfill, Bekasi, West Java, Indonesia. Landfill leachate samples are filtered to remove suspended particles and preserved at 4°C during transportation to the laboratory. Filtered leachate was used as a wastewater model to be treated, while AS was used for biological process experiments. The characteristic of the filtered leachate is given in Table 1.

Table 1. Characteristics of filtered landfill leachate.

Parameter	Value
Total Suspended Solids (TSS) (mg L^{-1})	36
Total Dissolved Solids (TDS) (mg L^{-1})	11.85
pH	8.50
BOD_5 (mg L^{-1})	3.91
COD (mg L^{-1})	4800
Chloride (Cl^-) (mg L^{-1})	1860
Dissolved Organic Carbon (DOC) (mg L^{-1})	1375
Inorganic Carbon (IC) (mg L^{-1})	1888

All reagents used in this research including iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$), iron (III) chloride ($FeCl_3$), ammonium hydroxide (NH_4OH), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), and sodium hydroxide (NaOH) were of analytical grade chemicals purchased from Merck.

2.2. Catalyst Preparation

CFA was modified into CFA catalyst (CFA/Fe) by incorporating Fe_3O_4 using an inverse co-precipitation technique (Niveditha and Gandhimathi, 2020). Ferrous sulphate and ferric chloride with a molar ratio of 1:2 M are called iron solutions dissolved in 30 mL of deionised water. Two grams of CFA were added to 60 mL of 10% NH_4OH and stirred. The iron solution was poured into the NH_4OH solution mixture with continuous stirring at 60°C and 450 rpm for 90 minutes until a black precipitate formed. The modified CFA catalyst was then filtered, rinsed several times, and dried overnight in an oven at 75°C.

2.3. Experimental Setup and Procedures

The Fenton reaction was conducted in a 250 mL glass batch reactor placed on a hotplate stirrer at room temperature of 30°C. Batch studies were conducted to determine the effect of operational conditions such as initial pH, catalyst (CFA/Fe) dosage and H_2O_2 dosage on landfill leachate treatment through the heterogeneous Fenton reaction. The initial pH of the leachate was adjusted using 6 M H_2SO_4 magnetic agitations and was maintained at 500 rpm. After the system reached the intended conditions, the initial sample (t=0 min) was collected, followed by the addition of the catalyst. A certain amount of oxidant (H_2O_2) is completely introduced at the beginning of the reaction. In the Fenton procedure, the reaction begins when an oxidant is introduced. The Fenton reaction was carried out for 120 minutes, then the sample was withdrawn, centrifuged, and filtered before further analysis.

The feasibility of coupling Fenton oxidation with the activated sludge process was evaluated by simulating biological treatment using Fenton-treated leachate and comparing the results with those obtained from untreated leachate. Prior to the experiment, suspended solids (SS) and volatile suspended solids (VSS) examinations were carried out to analyse solid and organic solid content in the AS. The pH of acidic leachate from Fenton process adjusted to neutral pH using 0.1 M NaOH. 300 mL of AS and 700 mL of leachate were added into a 2 L reactor equipped with a stirrer and an aerator as air supply. Aeration process was carried out for 8 hours of hydraulic retention time (HRT), following the typical aeration time applied in the Bantargebang Landfill. The samples were taken at regular intervals from the reactor and filtered prior to further analysis.

2.4. Analytical Methods

Colour content was measured with a UV-Vis Spectrophotometer (DR2000, HACH). Concentration of organic matter in the leachate sample was measured by total organic carbon (TOC) (TOC-L, Shimadzu). Residual hydrogen peroxide was estimated by metavanadate method using UV-Vis Spectrophotometer following the previous study by Nogueira *et al.* (2005). Iron leaching from the catalyst was also measured spectrophotometrically by Ferrover method (HACH Method No. 10249), while iron content in the catalyst was measured by APHA standard Method 3030E. All analyses were conducted in duplicate to improve measurement accuracy and reproducibility. The results were reported as average values. The surface morphology and element analysis were examined using scanning electron microscope (SEM) associated with an energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD) analysis.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

Morphological characterization of the CFA/Fe catalyst are shown in Figure 1. Previous studies by Niveditha and Gandhimathi (2020) found that unmodified CFA particles typically have a smooth surface texture and a notably spherical shape. In comparison to unmodified (CFA), catalyst CFA/Fe exhibits surface change after being augmented with Fe_3O_4. It showed distributed particles with an irregular flaky surface on the surface of the catalyst. As particle size decreases, a greater proportion of the particles are found at the surface catalyst. The smooth surface of material can limit the capability of pollutant adsorption when utilised as a heterogeneous catalyst. Adsorption has been recognized as an essential stage in catalytic processes, since adsorbed molecules generate intermediate surface complexes with higher reaction probability Soon and Hameed (2011). The addition of an NH_4OH solution to CFA results in partial structural modification, enhancing pore accessibility and volume (Kusumawardani and Purbasari, 2022). When Fe_3O_4 is added to CFA, granular Fe_3O_4 coating the CFA surface and densifies the catalyst surface. A rough solid surface created by Fe_3O_4 flakes will serve as the catalyst's active site.

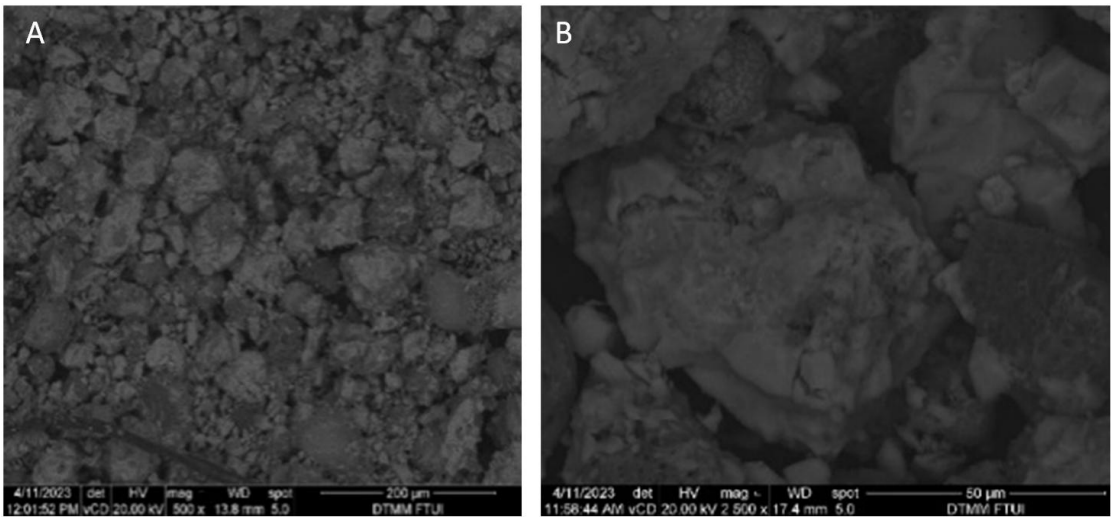

Figure 1. SEM Images CFA/Fe Catalyst of (a) 200µm and (b) 50 µm.

The elemental composition of the CFA/Fe catalyst is depicted in Table 2. It can be seen by weight percentage that the dominating elements in the catalyst CFA/Fe are Fe (49.71%), O (32.74%), Al (7.03%), and Si (6.67%). The presence of Fe and O components is due to the modification procedure, which raised the percentage of Fe_3O_4 in the catalyst, causing these two elements to dominate the catalyst composition. The presence of aluminium (Al) and silicon (Si)

reflects the fundamental composition of fly ash, in which Si and Al are the dominant elements (Mushtaq *et al.*, 2019). XRD patterns of CFA and catalyst CFA/Fe are presented in Figure 2. Diffraction peaks at approximately 2Θ = 26°, 31°, 43°, and 50° are typically associated with SiO_2 (quartz), Al-Si phases (mullite), and Fe_3O_4 (magnetite), although these phases appear less prominent in CFA (Niveditha and Gandhimathi, 2020). In CFA/Fe, distinct sharp peaks emerging at 35°, 43°, 57° and 62° can be attributed to Fe_2O_3 (hematite) and Fe_3O_4 (magnetite). The higher peak intensities observed after Fe loading indicate enhanced crystallinity. The observed enhancement verifies effective Fe incorporation and indicates potential improvements in catalytic efficiency and adsorption behaviour. Furthermore, determination of the total iron content in the CFA/Fe catalyst revealed an iron concentration of up to 328 mg g^{-1}.

Table 2. Elemental Composition of CFA/Fe Catalyst

Element	O	Mg	Al	Si	Ca	Ti	Fe	Mn
Wt. %	32.738	3.45	7.03	6.674	2.37	0.96	49.71	1.83
At %	57.77	3.725	6.976	6.336	1.67	0.53	25.8	0.88

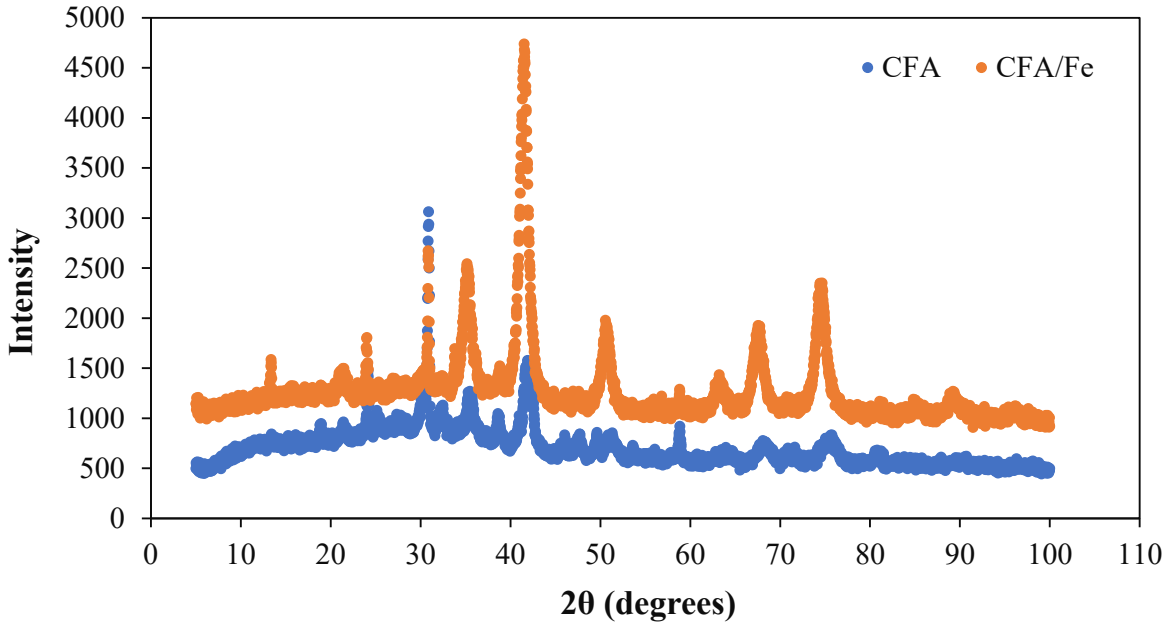

Figure 2. XRD profile of CFA Raw and CFA/Fe catalyst.

3.2. Effect of Catalyst Dosage

The effect of catalyst dosage on the degradation process was investigated by varying the catalyst dosages from 0.5 g L^{-1} to 3 g L^{-1} (Figure 3). The highest colour removal of 81.46% was obtained using 2 g L^{-1} of dosage of CFA/Fe catalyst. The effect of catalyst concentration illustrates that increasing the amount of catalyst enhances the surface area and active sites, which are responsible for the rapid decomposition of H_2O_2 (Adityosulindro *et al.*, 2018). However, enhancing the dose of catalyst in excess amounts (dosage 3 g L^{-1}) leads to a diminution in removal efficiency. The removal efficacy shrinks because iron ions react with hydroxyl radicals, resulting in a limitation on the number of active sites for oxidation and allowing the agglomeration of catalyst particles and excessive accumulation of iron (Mushtaq *et al.*, 2019; Niveditha and Gandhimathi, 2020).

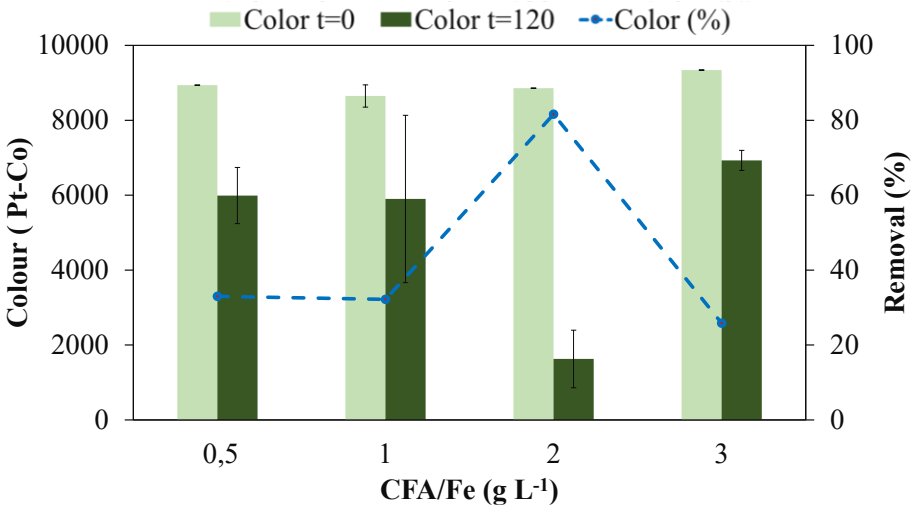

Figure 3. Effect of catalyst concentration on colour removal.
([H_2O_2] $_{initial}$= 4800 mg L^{-1} ; pH=3 ; T=30°C ; $V_{agitation}$ =500 rpm).

3.3. Effect of H_2O_2 Concentrations

In previous work, we have shown the potential contribution of the radical reaction by comparing Fenton reaction (CFA/Fe/H_2O_2) versus adsorption (CFA/Fe) (Simanjuntak *et al.,* 2023). In this study, the effect of H_2O_2 dosage on the Fenton process was investigated by varying the dosage from 0.25 to 2 times of the initial COD concentration of leachate, corresponding to 1200-9600 mg L^{-1} H_2O_2. The optimum operational parameter for the dosage of catalyst CFA/Fe 2 g L^{-1} was also used in these experiments. Figure 4 shows that the highest removal was obtained at variations [H_2O_2]:[COD] in concentrations 1:1 equal to 4800 mg L^{-1} H_2O_2. Conditions with H_2O_2 concentrations less than 4800 mg L^{-1} showcase no discrepancy in colour removal. This is probable because H_2O_2 is not only transformed selectively into •OH radicals but also can be degraded into H_2O and O_2 and/or exhausted through scavenging reaction (Ali *et al.*, 2013). Besides that, high and disproportionate amounts of H_2O_2 result in a scavenging reaction of H_2O_2 during the Fenton process whereas •OH radicals produced by the CFA/Fe catalyst react with excess H_2O_2 in the matrix rather than organic molecules of wastewater/landfill leachate. The scavenging reaction of •OH and H_2O_2 produces hydroperoxyl radicals (•OOH) and ($•O^{2-}$) (Hussain *et al.*, 2022). These radicals have a low oxidation potential, reducing elimination removal efficiency (Niveditha and Gandhimathi, 2020; Wang *et al.*, 2022).

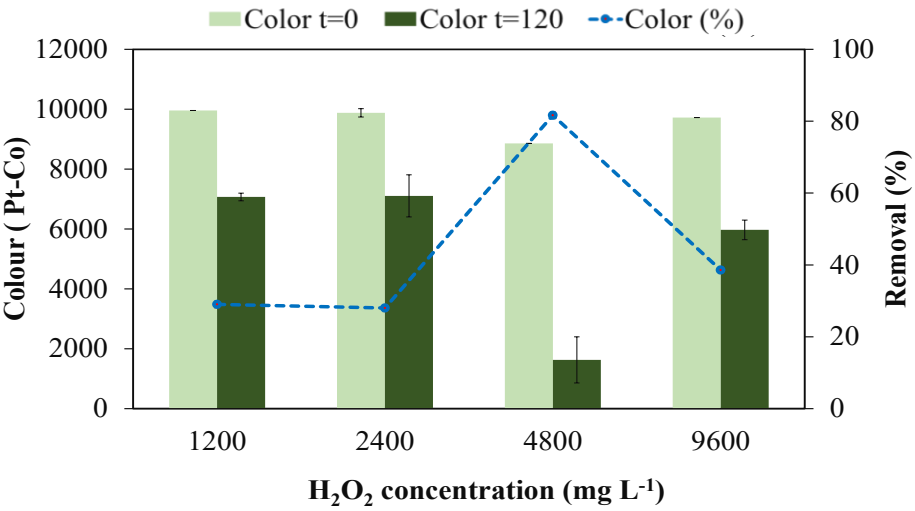

Figure 4. Effect of Oxidant Concentration on Colour Removal.
(pH =3; [CFA/Fe]=2 g L^{-1}; T=30°C; $V_{agitation}$ =500 rpm)

3.4. Effect of pH

pH is a vital metric in the Fenton process because it influences catalytic activity and the stability of H_2O_2 for the formation of hydroxyl radicals. Acidic pH was reported by various literatures for effective removal of pollutants (Adityosulindro *et al.*, 2022; Niveditha and Gandhimathi, 2020; Ribeiro *et al.*, 2017). Figure 5 illustrates that optimal decolourisation was attained at pH 3, reaching an efficiency of 81.46%. The highest removal efficiency was observed at pH 3, where iron ion dissolution enhanced degradation through a homogeneous Fenton-like mechanism. This result is consistent with the established mechanism of Fenton-based oxidation, in which mildly acidic conditions maximize H_2O_2 activation and hydroxyl radical generation, whereas increasing pH reduces the availability of catalytically active iron species because of hydrolysis and precipitation reactions (Hassani *et al.*, 2025). The acid matrix of pH 4 and pH 5 results in less colour elimination because the stability of dissolved iron can form Fe^{3+} and Fe^{2+}. The presence of Fe^{3+} favors the formation of iron hydroxide complexes. In addition, the solubility of Fe^{2+} decreases with increasing pH (Gopinathan *et al.*, 2022; Riadi *et al.*, 2021). In alkaline pH, iron ions precipitate, rendering the Fenton reaction between Fe and H_2O_2 impossible. Colour removal is achieved in an alkaline base through the adsorption mechanism of the CFA/Fe catalyst. Future studies are essential to compare the catalytic performance with unmodified CFA, homogeneous Fenton systems, and adsorption-only conditions in order to further elucidate the contribution of individual removal mechanisms.

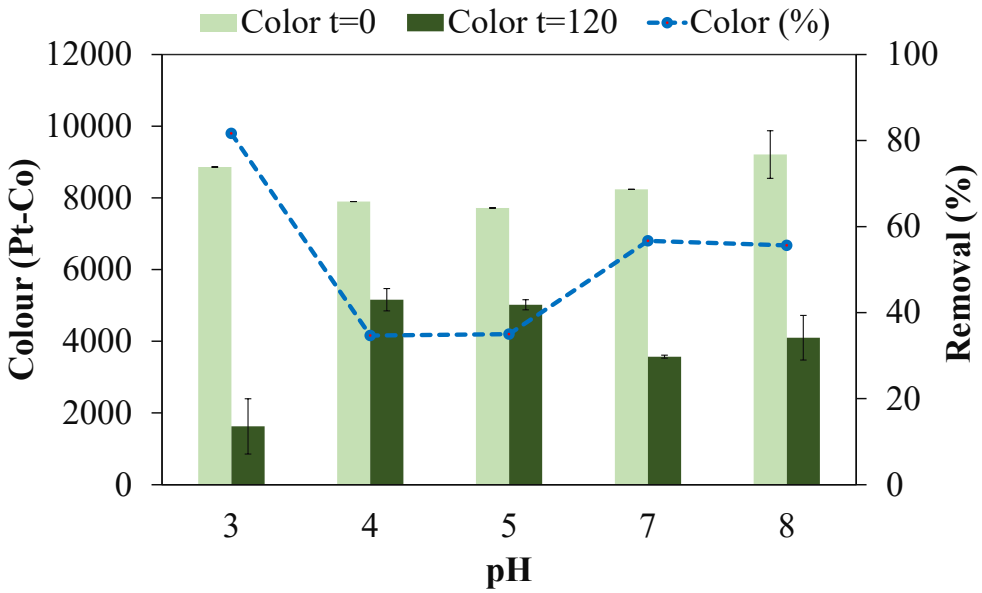

Figure 5. Effect of pH on colour removal.
([$H_2O_{2\ Initial}$] = 4800 mg L^{-1}; [CFA/Fe] =2 g L^{-1}; T=30°C; $V_{agitation}$ =500 rpm).

3.5. Performance of Iron Leaching Tests

Iron leaching tests were conducted under all parametric conditions of the Fenton process (Table 3). The assessment of iron leaching is essential since it not only reflects the stability of heterogeneous catalysts but also reveals the contribution of dissolved iron to the overall Fenton reaction mechanism. In the heterogeneous Fenton systems, iron leached from the solid catalyst could enter solution and trigger homogeneous Fenton reactions, thereby influencing the overall reaction pathway and serving as an indicator of catalyst stability (Thomas *et al.*, 2021). Dissolved iron ions released from heterogeneous catalysts may actively participate in homogeneous Fenton reactions, enhancing radical formation and contaminant breakdown; however excessive leaching also affects performance stability (Ścieżyńska *et al.*, 2023).

In the catalyst dosage experiment, the results of the iron leaching test revealed that the

percentage of iron leaching increases in direct proportion to the concentration of catalyst, with the total iron concentration observed between 12.4 and 23.6 mg L^{-1}. Iron leaching revealed a fluctuation trend with varying H_2O_2 concentrations. Iron leaching occurs due to the acidic matrix solution used in the process that enables iron to be expelled from the catalyst structure and dissolved in the matrix. This is owing to the nature of stable dissolved iron in solution with acidic pH, especially iron (II) or Fe^{2+}. The lowest iron leaching was obtained at the concentration of H_2O_2 with a ratio of 1x (4800 mg L^{-1}) with a total dissolved iron of 20.96 mg L^{-1}, and the highest iron leaching with a ratio of 2x (9600 mg L^{-1}) with a total dissolved iron of 47.80 mg L^{-1}.

Table 3. Performance of iron leaching test.

Experiment Variation	CFA/Fe	H_2O_2	pH	Colour Removal	Iron Leaching		
	(g L^{-1})	(g L^{-1})		(%)	(g L^{-1})	(%)	(Std. dev)
Catalyst Dosage	0.5	4800	3	33.00	12.40	5.02	0.92
	1	4800	3	32.20	17.70	7.17	0.52
	2	4800	3	81.64	20.90	8.46	0.86
	3	4800	3	25.80	23.60	9.55	0.92
H_2O_2 Concentration	2	1200	3	29.02	9.60	7.94	0.34
	2	2400	3	27.99	26.27	10.63	0.29
	2	9600	3	38.58	47.80	19.35	1.72
pH	2	4800	4	34.68	50.20	20.32	3.66
	2	4800	5	34.97	47.20	19.11	2.86
	2	4800	7	56.67	6.60	2.67	1.15
	2	4800	8	55.61	7.60	3.08	0.34

pH exerted the most pronounced effect on iron leaching. The highest iron leaching occurred at pH 4-5, reaching up to 50.20 mg L^{-1} (20.32%), indicating increased iron solubility and reduced precipitation in this pH range. In contrast, iron leaching sharply decreased at neutral to alkaline matrix (pH 7-8), with leached iron reaching only less than 8 mg L^{-1} or less than 5%. The observed low concentration reflects iron precipitation processes that restricted its dissolution into the aqueous matrix.

Iron leaching in this study is typically promoted under acidic conditions and elevated oxidant dosages, reflecting a balance between enhanced catalytic activity and catalyst stability (Nidheesh, 2015; Ścieżyńska *et al.*, 2023). In contrast, at neutral and alkaline pH, iron dissolution is significantly reduced, indicating improved catalyst stability due to iron hydroxide precipitation (Bouzayani and Sanromán, 2024). High iron leaching observed in this study, compared with typical heterogeneous Fenton systems, can also be attributed to the chloride-rich matrix of landfill leachate. Chloride ions not only scavenge hydroxyl radicals and shift the reaction pathway towards less reactive chlorine radicals, but also form stable Fe-Cl complexes that enhance iron solubility and promote catalyst dissolution (Gu *et al.*, 2025). This behaviour supports the concept of a hybrid heterogeneous-homogeneous mechanism, in which chloride-stabilized iron sustains the homogeneous cycle.

Although iron leaching was observed, the data in Table 3 show that assays with lower dissolved iron (<20%) still achieved higher removal efficiencies, indicating that CFA/Fe catalysis cannot be attributed solely to homogeneous reactions. Instead, the system operates via a hybrid mechanism, where surface-bound catalysis and dissolved iron cycles act

synergistically to enhance contaminant degradation.

Recent studies highlight that optimization approaches, including stepwise oxidant addition, are critical for maintaining process efficiency in high-chloride matrices and demonstrate that heterogeneous catalysts remain effective in treating concentrated leachates despite increased iron leaching (Li *et al.*, 2024; Méndez-Novelo *et al.*, 2025). These findings provide strong justification for integrating the Fenton process with biological AS treatment, as the oxidative pre-treatment enhances leachate biodegradability while the residual dissolved iron may function as an essential microbial cofactor, collectively improving the efficiency and robustness of the overall leachate treatment process (Wang and Qiao, 2024).

This study focused on single-cycle CFA/Fe application, and while iron leaching behavior was evaluated, catalyst reusability and regeneration potential were not assessed. The dissolution trends observed under acidic and chloride-rich conditions suggest that repeated use may lead to gradual catalyst deactivation. Although post-reaction analyses such as XRD, SEM, and FTIR of the spent catalyst were not conducted, the iron leaching results provide indirect insights into catalyst stability. Future work should therefore incorporate multi-cycle reuse experiments together with detailed post-reaction characterization to elucidate structural changes, surface morphology, and functional groups after repeated use, thereby clarifying catalyst deactivation pathways, regeneration potential, and long-term stability to establish the practical viability of CFA/Fe catalysts in landfill leachate treatment.

3.6. Assessment of Organic Removal

The highest percentage of colour removal in the Fenton process after varying operational parameters was obtained in experimental conditions with a catalyst concentration of 2 g L^{-1}, a concentration of H_2O_2 4800 mg L^{-1} and pH of 3 with 81.46% colour removal efficiency. Furthermore, organic matter degradation was investigated through the determination of DOC and total carbon TC. The leachate treated by the Fenton process exhibited DOC and TC concentrations of 783.93 mg L^{-1} and 784.8 mg L^{-1}, respectively, with an overall DOC reduction of 42.98%. The nearly identical DOC and TC values suggest effective elimination of DIC during the Fenton treatment, thereby leading to DOC with improved biodegradability potential, making it more amenable to subsequent biological treatment. DIC is defined as the sum of bicarbonate (HCO_3^-), carbon dioxide (CO_2), and carbonate (CO_3^{2-}). Liu *et al.* (2019) reported that wastewater treatment processes convert a substantial portion of organic carbon (OC) into CO_2, a significant fraction of which dissolves in the aqueous phase, typically leading to low pH values and high DIC concentrations in the treated wastewater.

Furthermore, the landfill leachate contained a high chloride concentration (1860 mg/L), which is known to scavenge hydroxyl radicals and generate less reactive chlorine radicals. Although direct quantification of chloride scavenging was not performed, the observed iron leaching behavior and moderate DOC removal efficiency suggest that chloride ions influenced the oxidation pathway by stabilizing dissolved iron and reducing •OH availability. Future work should incorporate radical probe assays or spectroscopic analyses to quantify the scavenging effect and the contribution of chlorine radicals to overall contaminant degradation.

3.7. Integration of Fenton Oxidation with Activated Sludge Process

A hybrid treatment approach was conducted to investigate the feasibility of the combined system Fenton oxidation followed by a biological activated sludge process (AS) to enhance organic removal. The treatment efficiency was evaluated by monitoring DOC removal during the activated sludge process. The characteristic of leachate after the Fenton oxidation step is as follows: COD = 4787 mg L^{-1}; DOC 653 mg L^{-1}; IC = 15 mg L^{-1}; pH = 3.6; total Fe = 24.4 mg L^{-1}; Residual H_2O_2 = 1979 mg L^{-1}. To establish suitable operating conditions for the activated sludge process (AS), the pH of the Fenton-treated leachate was adjusted back to neutral pH.

Figure 6 presents DOC profiles of both treated and non-treated leachates during an 8 h biological aeration. It was observed that the DOC removal efficiency was higher in normal AS (26.28% without Fenton) than in the pre-treated leachate (17.53% with Fenton pre-treatment).

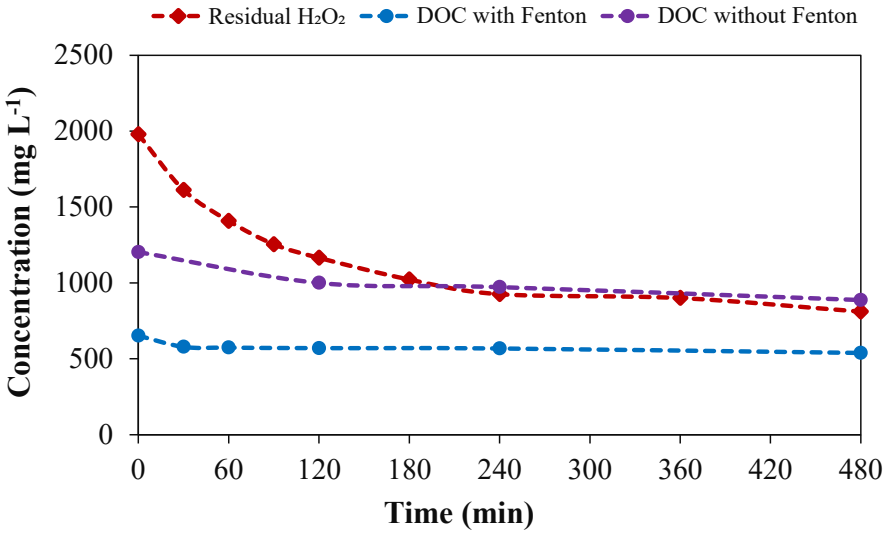

Figure 6. Effect of Fenton as pre-treatment of activated sludge process.

Performance of activated sludge process (AS) was further evaluated using the VSS/SS ratio, an indicator of active biomass content, with optimal values typically from 0.80 to 0.90 (Fan *et al.*, 2015). As shown in Figure 7, the VSS/SS ratio in AS increased from 0.62 to 0.76 after 8 h, while no appreciable change was observed in the Fenton–AS system. The lower DOC removal efficiency and unchanged VSS/SS ratio observed in the Fenton–AS system could be due to an inhibitory effect of Fenton reagents on microbial activity metabolism and growth. Residual H_2O_2 has been reported to induce oxidative stress in microbial communities, resulting in cellular membrane disruption, enzyme inactivation, and impairment of key metabolic pathways, thereby suppressing microbial activity, biomass development, and substrate utilization (Imlay, 2013; Liu and Tay, 2001). The stable VSS/SS ratio in the Fenton–AS system suggests limited biomass development, while the AS system without pre-treatment showed comparatively improved microbial activity, as reflected by increased VSS/SS ratios and DOC removal. These findings highlight the importance of controlling residual oxidants when integrating Fenton pre-treatment with the AS process.

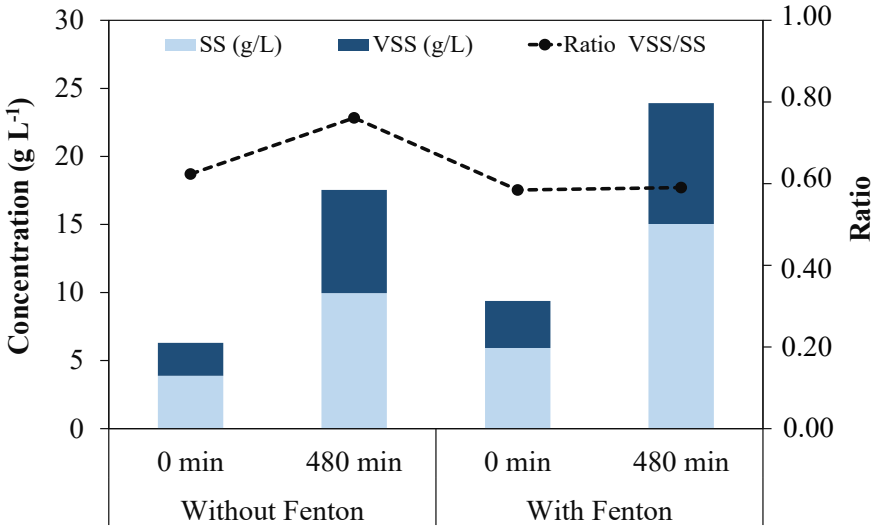

Figure 7. VSS and SS in the AS (without Fenton) and Fenton-AS (with Fenton) processes.

Although the ratio of BOD_5/COD was not determined in this study, the subsequent AS treatment provides useful insight into the biological treatability of the Fenton-pretreated leachate. The subsequent AS system served as a biological polishing step following heterogeneous Fenton oxidation, which is consistent with the concept of hybrid Fenton-based treatment approach (Hassani *et al.*, 2025), where biological treatment complements the partial oxidation achieved during the Fenton stage. In addition, the lower DOC removal of Fenton-AS accompanied by a relatively unchanged ratio of VSS/SS suggests the residual H_2O_2 and/or oxidation intermediates may temporarily suppress biomass development during the short-term biological treatment. Despite the relatively limited DOC removal and VSS/SS ratio observed in the Fenton–AS system, substantial hydrogen peroxide decomposition (up to 58%) was obtained. This finding implies a potential microbial adaptation to residual H_2O_2 or a beneficial effect associated with increased dissolved oxygen (DO**)** resulting from H_2O_2 decomposition (Nguyen *et al.*, 2015). Additionally, the considerable decomposition of residual H_2O_2 during the AS process indicates that the microbial consortia in the AS system remained metabolically active despite the presence of residual oxidants. Therefore, while the present results demonstrated the compatibility of the Fenton-pretreated leachate with subsequent AS treatment, quantitative evaluation of biodegradability and identification of specific oxidation byproducts require further studies.

4. CONCLUSIONS

The heterogeneous Fenton process using CFA/Fe catalyst showed promising results for landfill leachate treatment with colour removal ranging from 25.80 to 81.64% in 120 min reaction. The colour removal of landfill leachate increased with the increasing of catalyst and oxidant dosages until the optimum level, then tended to decrease. The highest colour removal of 81.46% was obtained with a catalyst dosage of 2 g L^{-1}, H_2O_2 4800 mg L^{-1}, and pH 3, with corresponding TOC removal up to 42.98%. Evaluation of iron leached in solution at the end of the reaction revealed total iron concentration in solution about 7.60-50.20 mg L^{-1}, corresponding to 3-20% of iron content in the catalyst. Although residual hydrogen peroxide has the potential to hinder the efficiency of subsequent activated sludge treatment, notable reductions in DOC and substantial decomposition of H_2O_2 were still achieved during the post-biological aeration stage. These findings indicate that microbial communities may develop adaptive responses to the presence of Fenton reagents when exposed over extended biological processing periods.

5. DATA AVAILABILITY STATEMENT

Data availability not informed.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

ADITYOSULINDRO, S.; JULCOUR, C.; BARTHE, L. Heterogeneous Fenton oxidation using Fe-ZSM5 catalyst for removal of ibuprofen in wastewater. **Journal of Environmental Chemical Engineering**, v. 6, n. 5, p. 5920–5928, 2018. https://doi.org/10.1016/j.jece.2018.09.007

ADITYOSULINDRO, S.; RAHDHANI, A.; HARTONO, D. M. Heterogeneous Fenton oxidation catalysed by rebar flakes waste for removal of methyl orange in water. **Journal of Applied Science and Engineering (Taiwan)**, v. 25, n. 3, p. 381–388, 2022. https://doi.org/10.6180/jase.202206_25(3).0003

ALI, M. E. M.; GAD-ALLAH, T. A.; BADAWY, M. I. Heterogeneous Fenton process using steel industry wastes for methyl orange degradation. **Applied Water Science**, v. 3, n. 1, p. 263–270, 2013. https://doi.org/10.1007/s13201-013-0078-1

BOUZAYANI, B.; SANROMÁN, M. A. Polymer-Supported Heterogeneous Fenton Catalysts for the Environmental Remediation of Wastewater. **Molecules**, v. 29, n. 10, p. 1–23, 2024. https://doi.org/10.3390/molecules29102188

DAO, D. S.; NGUYEN, N. V.; LE, S. T.; NGUYEN, H. K. D.; HOANG, H. V.; TRUONG, K. N. *et al.* Iron-Modified Fly Ash as Heterogeneous Fenton-Like Catalyst for Decolorization of Reactive Blue 182 Dye. *In*: PARKER, J. (ed.). **Fly Ash: Properties, Analysis and Performance.** Nova Science, 2017.

DENG, Y.; ZHAO, R. Advanced Oxidation Processes (AOPs) in Wastewater Treatment. **Current Pollution Reports**, v. 1, n. 3, p. 167–176, 2015. https://doi.org/10.1007/s40726-015-0015-z

FEIZI, R.; KAKAVANDI, B.; HASSANI, A.; GHANBARI, F. Treatment of landfill leachate via two-stage advanced oxidation processes: Photo-electrochemical activation of peroxymonosulfate and percarbonate/ozone/MnO2@carbon. **Journal of Water Process Engineering,** v. 82, p. 109416, 2026. https://dx.doi.org/10.1016/j.jwpe.2025.109416

FAN, J.; JI, F.; XU, X.; WANG, Y.; YAN, D.; XU, X. *et al.* Prediction of the effect of fine grit on the MLVSS/MLSS ratio of activated sludge. **Bioresource Technology**, v. 190, p. 51–56, 2015. https://doi.org/10.1016/j.biortech.2015.04.035

GOPINATHAN, P.; SANTOSH, M.S; DILEEPKUMAR, V. G.; SUBRAMANI, T.; REDDY, R.; MASTO, R. E. *et al.* Geochemical, mineralogical and toxicological characteristics of coal fly ash and its environmental impacts. **Chemosphere**, v. 307, n. May, p. 135710, 2022. https://doi.org/10.1016/j.chemosphere.2022.135710

GU, Z.; FANG, F.; HE, C.; CHEN, W. Effects of chloride ions on the transformation of dissolved organic matter in biologically treated waste leachate by a Fenton process. **Separation and Purification Technology**, v. 362, n. P1, p. 131321, 2025. https://doi.org/10.1016/j.seppur.2024.131321

HASSANI, A.; POURSHIRBAND, N.; SAYYAR, Z.; EGHBALI, P. Fenton and Fenton-like-based advanced oxidation processes. *In:* HAMDAOUI, O. (ed.). **Innovative and Hybrid Advanced Oxidation Processes for Water Treatment**. Elsevier eBooks, 2025. p. 171–203. https://doi.org/10.1016/b978-0-443-14100-3.00006-5

HOSSEINIKHAH, M.; GHALEBIZADE, M.; HASSANI, A.; BEHZADIAN, K. *et al.* An efficient sequential method for enhanced landfill leachate treatment and detoxification: Electrocoagulation/permanganate, peroxymonosulfate-based process, and electro-peroxone. **Journal of Environmental Management**. v. 388, p. 125785, 2025. https://doi.org/10.1016/j.jenvman.2025.125785

HUSSAIN, S.; ANEGGI, E.; MASCHIO, S.; CONTIN, M.; GOI, D. Steel Scale Waste as a Heterogeneous Fenton-like Catalyst for the Treatment of Landfill Leachate. **Industrial and Engineering Chemistry Research**, v. 60, n. 31, p. 11715–11724, 2021. https://doi.org/10.1021/acs.iecr.1c01901

HUSSAIN, S.; ANEGGI, E.; TROVARELLI, A.; GOI, D. Removal of Organics from Landfill Leachate by Heterogeneous Fenton-like Oxidation over Copper-Based Catalyst. **Catalysts**, v. 12, n. 3, p. 1–17, 2022. https://doi.org/10.3390/catal12030338

IMLAY, J. A. The molecular mechanisms and physiological consequences of oxidative stress: Lessons from a model bacterium. **Nature Reviews Microbiology**, v. 11, n. 7, p. 443–454, 2013. https://doi.org/10.1038/nrmicro3032

KARANAC, M.; ĐOLIĆ, M.; VELJOVIĆ, D.; RAJAKOVIĆ-OGNJANOVIĆ, V.; VELIČKOVIĆ, Z.; PAVIĆEVIĆ, V. *et al.* The removal of Zn^{2+}, Pb^{2+}, and As(V) ions by lime activated fly ash and valorization of the exhausted adsorbent. **Waste Management**, v. 78, p. 366–378, 2018. https://doi.org/10.1016/j.wasman.2018.05.052

KJELDSEN, P.; BARLAZ, M.A.; ROOKER, A. P.; BAUN, A.; LEDIN, A.; CHRISTENSEN, T. H. Present and long-term composition of MSW landfill leachate: A review. **Critical Reviews in Environmental Science and Technology**, v. 32, n. 4, p. 297–336, 2002. https://doi.org/10.1080/10643380290813462

KUSUMAWARDANI, R.; PURBASARI, A. Synthesis and Performance Evaluation of Magnetized Modified Coal Fly Ash as Adsorbent for Naphthol Blue Black Dye Removal from Synthetic Dye Wastewater. **Teknik**, v. 43, n. 3, p. 222–227, 2022. https://doi.org/10.14710/teknik.v43i3.48337

LASKAR, N.; SINGH, U.; KUMAR, R.; MEENA, S.K. Spring water quality and assessment of associated health risks around the urban Tuirial landfill site in Aizawl , Mizoram , India. **Groundwater for Sustainable Development**, v. 17, n. January, p. 100726, 2022. https://doi.org/10.1016/j.gsd.2022.100726

LI, P.; YIN, Z.; CHEN, C.; WANG, Y.; WANG, Y.; LIU, H. *et al.* Treatment of membrane-concentrated landfill leachate by heterogeneous chemical and electrical Fenton processes with Iron-loaded granular activated carbon catalysts. **Journal of Environmental Chemical Engineering**, v. 12, n. 2, p. 112337, 2024. https://doi.org/10.1016/j.jece.2024.112337

LIU, X.; YANG, X.; LI, Y.; ZANG, H.; ZHANG, L. Variations in dissolved inorganic carbon species in effluents from large-scale municipal wastewater treatment plants (Qingdao, China) and their potential impacts on coastal acidification. **Environmental Science and Pollution Research**, v. 26, p. 15019-15027, 2019. https://doi.org/10.1007/s11356-019-04871-2

LIU, Y.; TAY, J. Metabolic response of biofilm to shear stress in fixed-film culture. **Journal of Applied Microbiology**, v. 90, n. 3, p. 337–342, 2001. https://doi.org/10.1046/j.1365-2672.2001.01244.x

LOPEZ, A.; PAGANO, M.; VOLPE, A.; CLAUDIO, A.; PINTO, D. Fenton's pre-treatment of mature landfill leachate. **Chemosphere**, v. 54, p. 1005–1010, 2004. https://doi.org/10.1016/j.chemosphere.2003.09.015

MENDEZ-NOVELO, R. I.; ANDUZE, E. Z. C.; ESCALANTE-MANE, A. M.; VEGA-DE-LILLE, M. I.; RODRIGUEZ-GAMBOA, O. Y.; SAN-PEDRO, L. Treatment of landfill leachate: A three stage approach with Fenton process. **Journal of Water Process Engineering**, v. 79, n. October, 2025. https://doi.org/10.1016/j.jwpe.2025.108902

MUSHTAQ, F.; ZAHID, M.; BHATTI, I. A.; NASIR, S.; HUSSAIN, T. Possible applications of coal fly ash in wastewater treatment. **Journal of Environmental Management**, v. 240, n. March, p. 27–46, 2019. https://doi.org/10.1016/j.jenvman.2019.03.054

NGUYEN, N. T. N.; LE, V. T.; PHAM, K. L.; DUONG, V. H.; HOANG, T. N. Y.; LE, T. H. T. *et al.* Hydrogen peroxide as an extra oxygen source for activated sludge. **Journal of Science and Technology Vietnan**, v. 53, n. 3A, p. 97-102, 2015.

NIDHEESH, P. V. Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review. **RSC Advances**, v. 5, n. 51, p. 40552–40577, 2015. https://doi.org/10.1039/C5RA02023A

NIVEDITHA, S. V.; GANDHIMATHI, R. Flyash augmented Fe_3O_4 as a heterogeneous catalyst for degradation of stabilized landfill leachate in Fenton process. **Chemosphere**, v. 242, p. 125189, 2020. https://doi.org/10.1016/j.chemosphere.2019.125189

NOGUEIRA, R. F. P.; OLIVEIRA, M. C.; PATERLINI, W. C. Simple and fast spectrophotometric determination of H_2O_2 in photo-fenton reactions using metavanadate. **Talanta**, v. 66, p. 86–91, 2005. https://doi.org/10.1016/j.talanta.2004.10.001

PURWANTA, W.; SUSANTO, J. P. Laju Produksi dan Karakterisasi Polutan Organik Lindi dari TPA Kaliwlingi, Kabupaten Brebes. **Jurnal Teknologi Lingkungan**, v. 18, n. 2, p. 157, 2017. https://doi.org/10.29122/jtl.v18i2.2036

RAJ, R.; TRIPATHI, A.; DAS, S.; GHANGREKAR, M.M. Is waste-derived catalyst mediated electro-Fenton a sustainable option for mitigating emerging contaminants from wastewater? **Current Opinion in Environmental Science and Health**, v. 37, p. 100523, 2024. https://doi.org/10.1016/j.coesh.2023.100523

RIADI, L.; TANUWIJAYA, A. D.; JE, R. R.; ALTWAY, A. Fenton's Oxidation of Personal Care Product (PCP) Wastewater: A Kinetic Study and the Effects of System Parameters. **International Journal of Technology**, v. 12, n. 2, p. 298–308, 2021. https://ijtech.eng.ui.ac.id/article/view/4045

RIBEIRO, R. S.; RODRIGUES, R. O.; SILVA, A. M. T.; TAVARES, P. B.; CARVALHO, A. M. C.; FIGUEIREDO, J. L. *et al.* Hybrid magnetic graphitic nanocomposites towards catalytic wet peroxide oxidation of the liquid effluent from a mechanical biological treatment plant for municipal solid waste. **Applied Catalysis B: Environmental**, v. 219, p. 645–657, 2017. https://doi.org/10.1016/j.apcatb.2017.08.013

ŚCIEZYNSKA, D.; BURY, D.; JAKUBCZAK, M.; BOGACKI, J.; JASTRZEBSKA, A.; MARCINOWSKI, P. Waste iron as a robust and ecological catalyst for decomposition industrial dyes under UV irradiation. **Environmental Science and Pollution Research**, v. 30, n. 26, p. 69024–69041, 2023. https://doi.org/10.1007/s11356-023-27124-9

SIMANJUNTAK, S. M.; ADITYOSULINDRO, S.; MAULIDIANY, N. D. Evaluating Effectiveness of Modification Waste-derived Materials as Heterogeneous Fenton Catalyst: A Preliminary Study. *In:* INTERNATIONAL ENGINEERING STUDENT CONFERENCE, 8., 2023, Depok, West Java, Indonesia. **Proceedings[…]** Depok: Faculty of Engineering Universitas Indonesia, 2023. http://iesc.ui.ac.id/Proceedings2023.html

SOON, A. N.; HAMEED, B. H. Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process. **Desalination**, v. 269, n. 1–3, p. 1–16, 2011. https://doi.org/10.1016/j.desal.2010.11.002

TEE, P. F.; ABDULLAH, M. O.; TAN, I. A. W.; RASHID, N. K. A.; AMIN, M. A. M. *et al.* Review on hybrid energy systems for wastewater treatment and bio-energy production. **Renewable and Sustainable Energy Reviews**, v. 54, p. 235–246, 2016. https://doi.org/10.1016/j.rser.2015.10.011

THOMAS, N.; DIONYSIOU, D. D.; PILLAI, S. C. Heterogeneous Fenton catalysts: A review of recent advances. **Journal of Hazardous Materials**, v. 404, n. PB, p. 124082, 2021. https://doi.org/10.1016/j.jhazmat.2020.124082

TRIHADININGRUM, Y.; WILUJENG, S. A.; TAFAQURY, R.; RADITA, D. R.; RADITYANINGRUM, A. D. Evidence of microplastics in leachate of Randegan landfill, Mojokerto City, Indonesia, and its potential to pollute surface water. **Science of the Total Environment**, v. 874, n. February, 2023. https://doi.org/10.1016/j.scitotenv.2023.162207

WANG, C.; JIANG, R.; YANG, J.; WANG, P. Enhanced Heterogeneous Fenton Degradation of Organic Pollutants by CRC/Fe_3O_4 Catalyst at Neutral pH. **Frontiers in Chemistry**, v. 10, n. April, p. 1–8, 2022. https://doi.org/10.3389/fchem.2022.892424

WANG, J.; QIAO, Z. A comprehensive review of landfill leachate treatment technologies. **Frontiers in Environmental Science**, v. 12, n. September, 2024. https://doi.org/10.3389/fenvs.2024.1439128

XU, F.; LU, Q.; LI, K.; ZHU, T.T.; WANG, W.K.; HU, Z. H. Green synthesis of magnetic mesoporous carbon from waste-lignin and its application as an efficient heterogeneous Fenton catalyst. **Journal of Cleaner Production**, v. 285, p. 125363, 2021. https://doi.org/10.1016/j.jclepro.2020.125363

YE, G.; ZHOU, J.; HUANG, R.; KE, Y.; PENG, Y.; ZHOU, Y. *et al.* Magnetic sludge-based biochar derived from Fenton sludge as an efficient heterogeneous Fenton catalyst for degrading Methylene blue. **Journal of Environmental Chemical Engineering**, v. 10, n. 2, p. 107242, 2022. https://doi.org/10.1016/j.jece.2022.107242