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Case Report

Carwash wastewater treatment through the synergistic efficiency of microbial fuel cells and metal-organic frameworks with graphene oxide integration

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ABSTRACT

This study explored the effectiveness of integrating Microbial Fuel Cells (MFC) with Metal-Organic Frameworks (MOF) enhanced by graphene oxide as a unique approach for carwash effluent treatment. The research encompassed three key components: analyzing MFC in isolation, evaluating MOF alone, and studying the combined MFC and MOF approach. The results demonstrated that the simultaneous use of MOF and MFC led to significant improvements in pollutant removal, indicating a synergistic effect on various pollutants within the wastewater. In retrospect, the MFC displayed low power density (0.095 mW/m^2) and current density (2.8 mA/m^2) during the initial 2 hours. However, a significant increase occurred, peaking at 46.2 mA/m2 and 21.62 mW/m^2 by the 18th hour. Although current density decreased thereafter, power density stayed relatively high, indicating stabilization of microbial activity. The 48-h experiment concluded with 17.4 mA/m^2 and 11.28 mW/m^2. Notably, the combined MOF and MFC treatment consistently outperformed individual treatments, especially in the removal of heavy metals like zinc, nickel, and cadmium, with zinc removal rates increasing from 92.6 % to 96.5 %. In terms of organic contaminants, the integrated treatment approach achieved a remarkable 99.2 % removal of Biochemical Oxygen Demand (BOD). Moreover, the integrated treatment approach achieved a remarkable 100 % removal efficiency for turbidity and TSS, resulting in improved water clarity due to better fine suspended particle removal facilitated by MFC. The findings suggest that the combination of MOF and MFC holds great potential for comprehensive wastewater treatment, effectively eliminating a range of contaminants, including organic compounds, heavy metals, and general water quality parameters. The practical application of this integrated method can be further optimized and expanded through additional research and system refinement.

1. Introduction

Despite the undeniable utility of automobiles, they require regular cleaning, a process that consumes a substantial amount of water. According to research, different car washes use different amounts of water—150 L at the lowest and 600 L at the highest—with an average of 200 L per car [1]. As a result, each carwash facility uses roughly 10,000 L every day [1]. The large amount of water required for automobile washing is also associated with the production of large amounts of wastewater, which is comprised of a wide range of contaminants [2]. Therefore, carwash effluent poses environmental challenges due to various pollutants, including hydrocarbons, oils, grease, total suspended solids (TSS), copper (Cu), zinc (Zn), surfactants, detergents, turbidity, total dissolved solids (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbons (TOC), and phosphates. These pollutants can negatively impact aquatic ecosystems,

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leading to reduced oxygen levels, harm to aquatic life, impaired photosynthesis, hindered plant growth, and increased salinity. The industry faces significant challenges in treating carwash wastewater, emphasizing the urgent need for innovative, efficient, and cost-effective treatment solutions to mitigate environmental risks associated with these pollutants. Currently, existing treatment methods for carwash effluent involve several approaches to mitigate the impact of pollutants. Common methods include sedimentation or settling tanks to remove larger particles, filtration systems to capture suspended solids, and oil-water separators to separate oils and greases. Additionally, biological treatment processes, such as activated sludge systems, are employed to break down organic pollutants through microbial activity [3]. Chemical treatment methods may involve the use of coagulants and flocculants to aid in the removal of suspended particles. Some typical and widely used treatment methods for carwash wastewater are electrocoagulation [4,5] and membrane filtration, [6,7]. While these conventional methods are effective to some extent, challenges persist in addressing the diverse range of pollutants found in carwash effluent comprehensively. This limitation necessitates the exploration of advanced treatment approaches, such as the integration of Microbial Fuel Cells (MFC) with Metal-Organic Frameworks (MOF), enhanced by graphene oxide, which holds promise for achieving more efficient and sustainable wastewater treatment. The following section details the unique advantages and synergistic effects of the MOF + MFC approach in enhancing pollutant removal and overall treatment efficacy.

As previously highlighted, despite the fact that a number of treatment strategies have been established, these approaches frequently have shortcomings or restrictions, such as high operational costs, inefficient removal, or the production of secondary waste. A viable strategy for the sustainable treatment of car wash wastewater is the combination of microbial fuel cells (MFCs) with composite metal-organic frameworks improved by graphene oxide. Nevertheless, the current body of research in this area falls short of providing a thorough grasp of the capabilities and performance of these interconnected systems. The purpose of this study is to fill in these gaps by examining the efficacy of this novel treatment strategy, which provides a long-term resolution to an environmental issue. Because of graphene oxide's special qualities [8], such as its huge surface area and strong adsorption capacity, it is a great option to improve MOFs' ability to capture contaminants such as organic compounds, heavy metals, and surfactants [9]. The composite material that results from the integration of graphene oxide into MOF structures has better adsorption properties. These graphene oxide-enhanced MOFs bind pollutants to their surface by a combination of physical adsorption and chemical interactions, therefore capturing the pollutants in wastewater. This procedure helps to effectively treat wastewater by drastically lowering the amount of contaminants in the wastewater [10]. Microbial fuel cells (MFCs) are incorporated to improve the treatment process even more. MFCs use the energy produced by microbial metabolism to power the MOFs' increased MOFs' adsorption and removal of contaminants. MFCs use microorganisms' metabolic processes to break down organic materials found in wastewater [11]. When the organic chemicals are consumed by the microorganisms, which are mainly bacteria, they release electrons in the process. The MFC then gathers these electrons and transfers them via an external circuit to produce an electric current [12,13]. There are several uses for this electricity, one of which is to power the therapy procedure. In addition, microbes' decomposition of organic materials lowers the organic load in wastewater, thereby treating it [14]. Additionally, MFCs can aid in the removal of BOD and COD, which are markers of the degree of organic pollution in wastewater. Therefore, by fusing microbial metabolism with electricity generation, MFCs provide a sustainable, energy-efficient, and ecologically beneficial means of treating wastewater [15].

It is important to note that the treatment of carwash effluent poses a significant environmental challenge, requiring innovative and efficient methods to address the complex mix of pollutants. While existing studies have explored various approaches, a notable gap exists in the exploration of integrated technologies, particularly the combined utilization of Microbial Fuel Cells (MFC) [16,17] and Metal-Organic Frameworks (MOF) enhanced by graphene oxide. This study seeks to fill this crucial gap by systematically analyzing the individual contributions of MFC and MOF, as well as investigating the synergistic effects of their combined application. By doing so, we aim to not only enhance our understanding of these technologies' capabilities in isolation but also to uncover novel insights into their collaborative potential for achieving comprehensive and sustainable carwash effluent treatment. In addition to addressing the research gap, this study holds substantial importance for both society and industry. On a societal level, effective carwash effluent treatment is imperative for safeguarding environmental health and water resources. By exploring innovative approaches like the integration of Microbial Fuel Cells (MFC) and Metal-Organic Frameworks (MOF) enhanced by graphene oxide, this research contributes to the development of sustainable solutions for wastewater management. Successful implementation of these technologies can significantly reduce the environmental impact of carwash operations, ensuring cleaner water discharge into ecosystems and promoting overall environmental sustainability. From an industrial perspective, the findings of this study offer a valuable roadmap for optimizing wastewater treatment processes in the carwash industry. The integration of MFC and MOF presents a novel and potentially more efficient method, which not only enhances pollutant removal but also has the potential to reduce operational costs and resource consumption. Industry stakeholders can benefit from the insights gained in this study by adopting more environmentally friendly practices, meeting regulatory standards, and potentially improving their overall operational efficiency. Thus, the study not only contributes to scientific knowledge but also has practical implications for advancing sustainable practices in both society and industry.

In light of this knowledge, the present study investigated the viability of treating carwash wastewater by means of a composite MOF and a microbial fuel cell. To be more specific, the primary objective of this study is to investigate the efficacy of integrating Microbial Fuel Cells (MFC) with Metal-Organic Frameworks (MOF) enhanced by graphene oxide for the treatment of carwash effluent. Specifically, the study aims to assess the individual contributions of MFC and MOF, as well as the synergistic effects of their combined application, in order to enhance pollutant removal efficiency. The purpose of this research is to advance our understanding of sustainable and comprehensive wastewater treatment methods, particularly in the context of carwash effluent, and to contribute valuable insights that can inform the development of more effective and environmentally friendly treatment technologies for this specific type of wastewater. A dearth of thorough studies has been conducted on the efficacy of MOFs in treating complex wastewater streams, and the integration of cutting-edge materials like graphene oxide into MOFs and their combination with MFCs remains a mostly unexplored subject. Furthermore, even though the research on graphene-based materials and MFCs for wastewater treatment is expanding, nothing is known about the potential benefits of merging these technologies. It is worth noting that, the treatment of carwash effluent is a pressing environmental concern given its complex pollutant composition. Existing methods, while effective to some extent, face limitations in comprehensively addressing the diverse array of contaminants present in carwash wastewater. This study aims to address this critical gap by exploring an innovative approach - the integration of Microbial Fuel Cells (MFC) with Metal-Organic Frameworks (MOF) enhanced by graphene oxide. The inadequacies of current treatment methods underscore the need for advanced, sustainable solutions that can simultaneously target various pollutants in carwash effluent. By delving into the synergistic effects of MOF + MFC technology, this research seeks to contribute significantly to the development of more efficient and environmentally friendly carwash effluent treatment methods. By investigating the potential of this cutting-edge hybrid system to provide a sustainable and energy-efficient solution for carwash wastewater treatment, this study aims to close this knowledge gap. This project is to assist in the development of economical and ecologically appropriate strategies to manage the growing load of wastewater pollution in urban contexts by tackling the current challenges in wastewater treatment.

2. Materials and methods

2.1. Adsorbent material preparation

Using a precise phase inversion technique, the study constructed polymeric composite beads consisting of Zeolitic Imidazolate Framework-8 (ZIF-8) and Polyethersulfone (PES) in the synthesis procedure. The process started with preparation of a polymeric solution. To be exact, 5.5 g of N,N-Dimethylacetamide (DMAc) solvent were carefully mixed with 1.5 g of PES and 0.5 g of Polyvinylpyrrolidone (PVP). This mixture was then blended for a full day at a regulated room temperature of 25 °C to provide the best possible solubility and uniformity of the polymers. Additionally, 1.5 g of Zeolitic Imidazolate Framework-8 (ZIF-8) materials were dispersed with the highest precision. The polymeric solution was then methodically added to pure water using an automated pump, guaranteeing the most precise drop-by-drop dispensing procedure. This methodical procedure ensured that the composite beads formed without a hitch, clearly demonstrating that the phase inversion process was successfully completed.

After synthesis, these composite beads were subjected to a regulated drying process to improve their properties. The drying process was conducted in a temperature-controlled, well-regulated atmosphere with a consistent 40 °C. In order to make sure that no degradation occurred, the glass transition temperature of the polymer and the thermal stability of the MOF components were taken into consideration. Because the drying process lasted precisely 12 hours, there was less chance of defects and more uniform drying. The synthetic composite beads were characterised using scanning electron microscopy (SEM) (ZEISS, Oberkochen, Germany). By providing a comprehensive understanding of the structure and composition of the beads, this characterization method boosted the trustworthiness of the data.

As part of the GO dispersion procedure, GO was evenly disseminated in deionized water using a sonication process that took around 4 h and used a sonication power of 150 W. For GO to be properly incorporated into the composite, a stable and uniformly distributed GO solution had to be created. As the GO dispersion was blended with the PES-ZIF combination, it was progressively added while swirling continuously at a regulated speed of 300 RPM. The amount of GO added was controlled to generate a concentration of 5 % (w/w) in relation to the other components, in accordance with the desired properties for the composite beads. Additionally, the homogeneity of the composite material was achieved methodically. To guarantee even dispersion, mechanical stirring was employed for a further 2 h. Following that, 30 minutes of ultrasonication were performed using a high-frequency probe sonicator (Hielscher Ultrasonics, Oderstraβe, Germany) set to operate at 40 kHz. After that, high-shear mixing was carried out for 15 minutes at 10,000 RPM using a high-speed homogenizer. In order to ensure that GO was smoothly integrated with the other composite components and produced a properly blended and homogenous product, these exact processing processes were crucial.

2.2. Experimental setup

2.2.1. Graphene oxide-enhanced composite metal-organic frameworks

The experiment on continuous flow adsorption was carried out in a well-built column with a depth of 16 cm (Fig. 1). The produced adsorbent material, which had a size of 2 mm each, was poured into the filter depth in order to achieve the required bed height. During the experiment, a layer of cleverly placed 1-mm glass beads was used to support both ends, ensuring the integrity of the adsorbent beads and preventing them from being washed away. Throughout all experimental settings, the flow rate was kept constant at 2 mL per minute, ensuring accuracy and consistency. It is noteworthy that the coloured wastewater was pretreated using an adsorption procedure conducted in an ultrasonic device. The treated wastewater was then continually added to the column using an upward flow configuration that was powered by an accurate peristaltic pump. Samples from the column's effluent location were collected at different intervals. After that, these samples underwent a comprehensive analysis using suitable and advanced analytical techniques to accurately quantify and assess their concentrations. Fig. 1

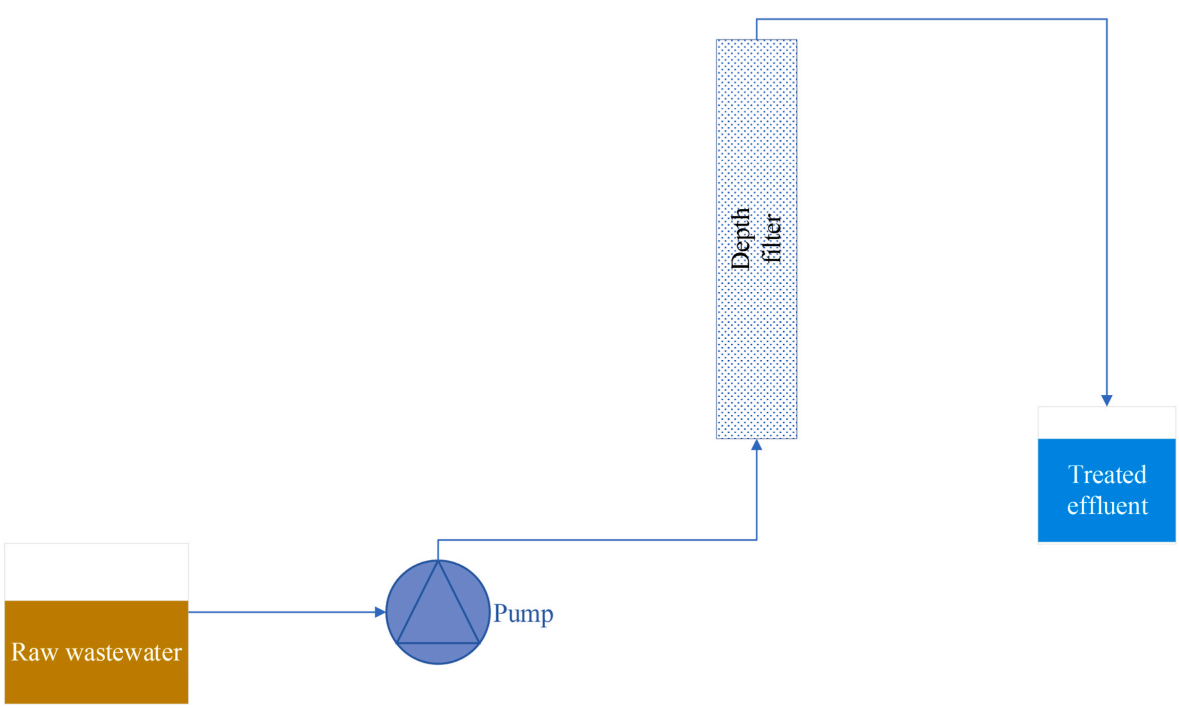


Fig. 1. MOF treatment system.

gracefully illustrates the general idea and configuration of this continuous adsorption method, offering a perceptive pictorial depiction of the testing.

2.2.2. MFC experimental setup

This combination increased the MFC's efficiency in eliminating pollutants while utilising its innate ability to produce energy. The integration in question presents a noteworthy opportunity to salvage valuable resources from the wastewater processed, augmenting the process's sustainability. Concurrently, an additional study entailed building a double-chamber MFC (refer to Fig. 2). Two independent chambers, one for the anode and the other for the cathode, made up this MFC arrangement. A salt bridge that allowed protons to move from the anode to the cathode chamber efficiently provided the vital link between these chambers. The target wastewater was poured into the anode chamber of the experimental setup, and tap water was poured into the cathode chamber. The anode and cathode chambers were placed 20 cm apart and were separated by a proton exchange membrane. Uncoated graphite flats that were 5 cm by 2 cm were used as the anode and cathode electrodes. The anode and cathode electrodes in the reactor were linked by copper wires. The effective transfer of electrons was ensured by the 100-Ω resistance of these cables. The electrodes underwent a 24-h pretreatment with deionized water prior to the start of the pilot experiment. The anode segment received the addition of the inoculum, while the cathode compartment received the introduction of the substrate. For 72 hours, this MFC was used to test the production of power. To measure the production of electricity, these steps were repeated for different possible electroactive bacteria and abiotic controls.

The anode and cathode were connected with a coated copper wire, and a resistor was added to finish the electrical circuit (Fig. 2). The anode and cathode were both expertly crafted from zinc and copper, respectively, and had the same surface area of 0.0027 square metres. Using glass sheets that could be found locally, the chambers were painstakingly built to measure 0.25 m in length, 0.10 m in width, and 0.20 m in height. In order to guarantee a safe passage between the rooms, a salt bridge made of agar was deliberately used. This bridge was painstakingly made by immersing surgical linen in a 0.1 M agar solution and then covering it with a 4.0 cm long by 0.5 cm diameter PVC pipe. Every connection in the MFC system was completely sealed with M-seal to thwart any possible leaks, underscoring the dedication to accurate experimentation and efficient data collection. A constant hydraulic retention duration of 150 minutes was used for all studies.

2.3. Inoculation of microorganisms and the collection of anolyte

A broad spectrum of microorganisms, including *Escherichia coli*, *Anabaena, Rhodospirillum*, and *cyanobacteria*, were employed in the study. The initial step of this microbial investigation involved collecting organic-rich benthic microbes from a nearby pond, establishing the foundation for further research. These microorganisms underwent meticulous cultivation through a carefully devised procedure to create optimal developmental conditions. This cultivation process entailed blending 1.5 % cow dung and 0.4 % sugar with the gathered benthic organisms, resulting in a nutrient-rich medium conducive to their growth. Subsequently, this nutrient mixture was placed in an anaerobic environment for 48 hours, providing the microbes with an atmosphere conducive to growth and preparation for their crucial roles in the experimental setup. With the cultured microbes now prepared for interaction, attention shifted to the anode chamber, which served as the central hub of the experiment.

2.4. Investigation of electrical current and power density

While keeping an eye on the microbiological activity inside the MFC, the research also investigated current and power density. It is imperative to stress that the electrical output in MFCs, which is a reflection of the metabolic activity of the microorganisms involved in the breakdown of pollutants, is closely linked to the effectiveness of pollutant removal. Generally speaking, more electrical output indicates more microbial activity, which correlates to better contaminants being removed from the substrate or effluent. This connection arises from the fact that the microbes that produce energy also frequently act as bio-catalysts in the breakdown of organic contaminants. Consequently, increased electrical output in MFCs usually translates into increased efficiency in the removal of pollutants, making MFCs an inventive and long-lasting technology for the treatment of wastewater as well as the generation of clean energy.

Using the cell voltage and a constant external resistance of $R = 100Ÿ$, we applied Ohm's law to determine the current. The study used a digital

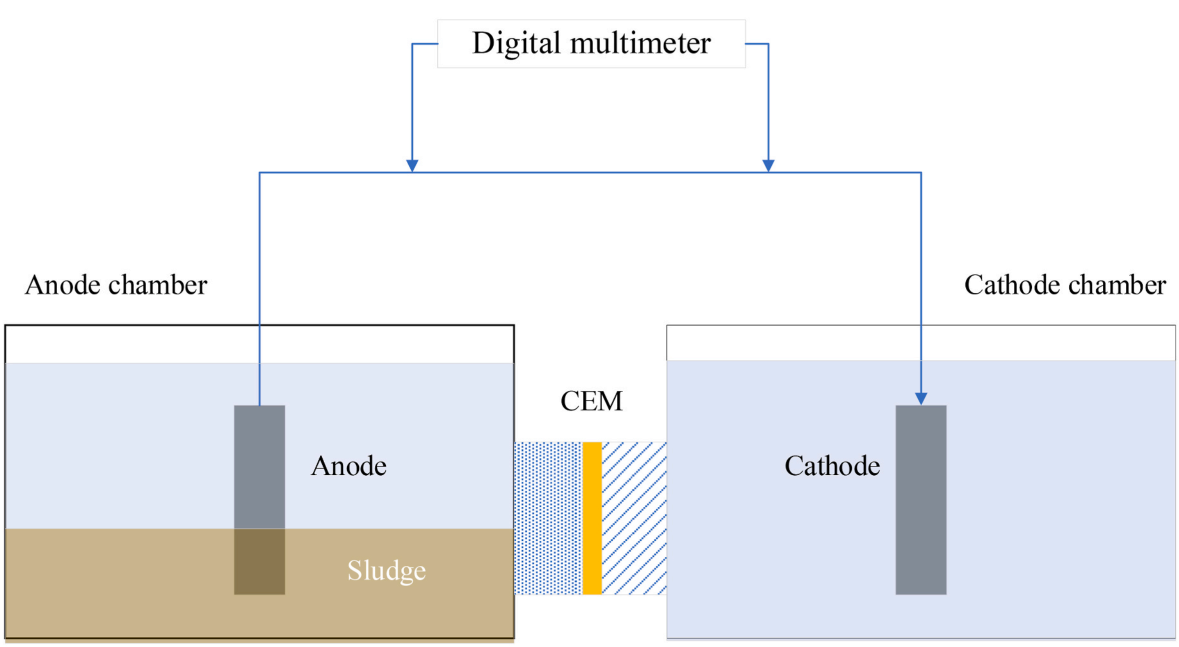


Fig. 2. MFC system schematic diagram.

multimeter (UK-831LN) that was safely linked to the MFC using crocodile clips in order to record the cell voltage data. To guarantee the accuracy and dependability of the data collecting procedure, these voltage measurements were painstakingly made and recorded in millivolts (mV) during a continuous 48-h period. Equation (1) provides a succinct summary of the procedure used to calculate power density.

$$P = \frac{V_t^2}{A \times R_s} \quad \text{(Equation 1)}$$

For the sake of this discussion, P is the power density in milliwatts per square metre (mW/m^2), Vt is the output voltage in millivolts (mV), A is the surface area of the anode in square centimetres (cm^2), and Rs is the external resistance in ohms ().

2.5. The employed analytical methods

The study investigated a number of water quality parameters from the raw wastewater and treated effluent samples. Sophisticated experimental techniques were used, including Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), for the analysis of zinc (Zn), total hardness, calcium, manganese, fluorides, nickel, and cadmium. Particular reagents designed to ensure the precision of assays were used and these approaches allowed the study to precisely estimate the concentration levels in the samples. Moreover, other analytical techniques, such as ion-selective electrodes and colorimetric techniques were used to investigate nitrates, cyanides, lead, and arsenic. Sulfanilamide, barbituric acid, and sodium borohydride were among the reagents that were helpful in establishing the reactions required for precise quantification of these potentially toxic elements.

The examination of TSS and TDS in the samples proved effective through the application of physical assessments, incorporating filtration, gravimetric analysis, and evaporation methods. The study employed colorimetric analysis using the Nessler reagent in conjunction with the Kjeldahl method to quantify both total nitrogen (TN) and ammonia-nitrogen (NH_3–N). Sulfuric acid, complex-forming agents, and catalysts were among the reagents used to make nitrogen compound conversion and measurement easier. The concentrations of total phosphorus (TP) were measured using colorimetry after a digestion procedure. Ammonium molybdate and ascorbic acid were among the reagents used to produce a visible complex that allowed for precise measurement. By extracting these materials from the wastewater with the aid of a solvent, gravimetric methods were utilised to quantify the amount of fats, oils, and grease (FOG). Accurate readings were obtained by weighing the residual solid leftovers afterwards.

For copper (Cu), surfactants, and electrical conductivity (EC), the study employed kits and instruments made specifically for each parameter. A conductivity metre was used to measure electrical conductivity directly. Like other heavy metals, copper concentrations were measured using the ICP-MS, and surfactant quantification was done with particular test kits that included reagents like dye solutions and colour charts for precise measurements. Nevertheless, the study employed a variety of techniques to measure turbidity, total organic carbon (TOC), chemical oxygen demand (COD), and biochemical oxygen demand (BOD). Without the use of special reagents, turbidity measurements were carried out with a turbidimeter, concentrating on the light scattering by water particle content. Colorimetric tests were employed in COD analysis to quantify organic matter oxidation using reagents such as sulfuric acid and potassium dichromate. The samples were incubated with microorganisms for the duration of the BOD analysis, and the sample's drop in dissolved oxygen was tracked. Ultimately, high-temperature combustion or wet oxidation procedures were used to determine TOC, with chemicals such as persulfate being used to aid in sample digestion.

2.6. Integrated approach

Fig. 3 delineates the sequential stages of the proposed Carwash Wastewater Treatment methodology, leveraging the synergistic efficiency of MFC MOF with graphene oxide integration. The process initiates with an initial assessment, involving the evaluation of carwash effluent composition and identification of key pollutants along with their concentrations. Subsequently, the MFC is isolated for an individual analysis, encompassing the measurement of power and current density over time. A parallel analysis is conducted for the MOF, evaluating its efficiency in pollutant removal. The integration phase combines the simultaneous use of MFC and MOF, allowing for the monitoring of synergistic effects on pollutant removal.

2.7. Adsorption capacity

The Langmuir adsorption isotherm, a popular model for characterising adsorption processes, wsa used to assess the adsorption capacity of the adsorbents. To be more specific, Equation (2) was used to express the Langmuir isotherm.

$$q = \frac{Q \times b \times C}{1 + b \times C} \quad \text{(Equation 2)}$$

q (adsorption amount) is expressed in units such as moles of gas adsorbed per gram of adsorbent (mol/g) or milligrams of gas adsorbed per gram of adsorbent (mg/g). Q is the maximum adsorption capacity (often expressed in mass per unit mass of the adsorbent); is expressed in the same units as q, C is the equilibrium concentration of the adsorbate in the solution; is expressed in units of moles per unit volume (mol/L or mol/m^3), and b is the Langmuir constant associated with the adsorption energy; (Langmuir adsorption equilibrium constant) is often reported in units of L/mol or m^3/mol, depending on the units used for concentration C. It is important to note that, monolayer adsorption onto a homogenous surface with a finite number of identical adsorption sites is assumed by the Langmuir model. The maximal adsorption capacity Q and the Langmuir constant b can be estimated by fitting experimental data of adsorption isotherms (the connection between q and C) to the Langmuir equation. These parameters include important details regarding the performance of the adsorbent, including its capacity to adsorb the particular adsorbate and the ideal conditions for adsorption.

2.8. Computation and aggregation of indices

As part of the water quality analysis, Water Quality Indices (WQIs) were developed in this study based on the water quality parameters of interest. It is also worth noting that, WQIs could not be developed without first producing a complete list of 24 distinct water quality parameters. Using the WQI approach simplified the evaluation of treatment methodsinvestigated in this study. Equation (3) through (6) provide an explanation of the step by step procedures used to develop the WQIs. During the first phase, each parameter was given a unique weight (w_i) on a scale ranging from 0 to 10, which indicated how much of an impact it had on the quality of the water (with drinking water quality as a reference). A score of 0 indicated no effect at all, while a score of 10 indicated a significant effect (Table 1).

The National Sanitation Foundation's Water Quality Index served as an inspiration for these weight allocations, which were based on the relative importance of the various water quality parameters for the purposes for which they were intended [18]. Equation (3) [19,20] was used to calculate the relative weight (R_w) by dividing the weight of each parameter by the sum of all given weights.

$$R_w = \frac{g_i}{\sum_{i=1}^{n} g_i} \quad \text{(Equation 3)}$$

Whereby; 'n' stands for the total number of parameters taken into

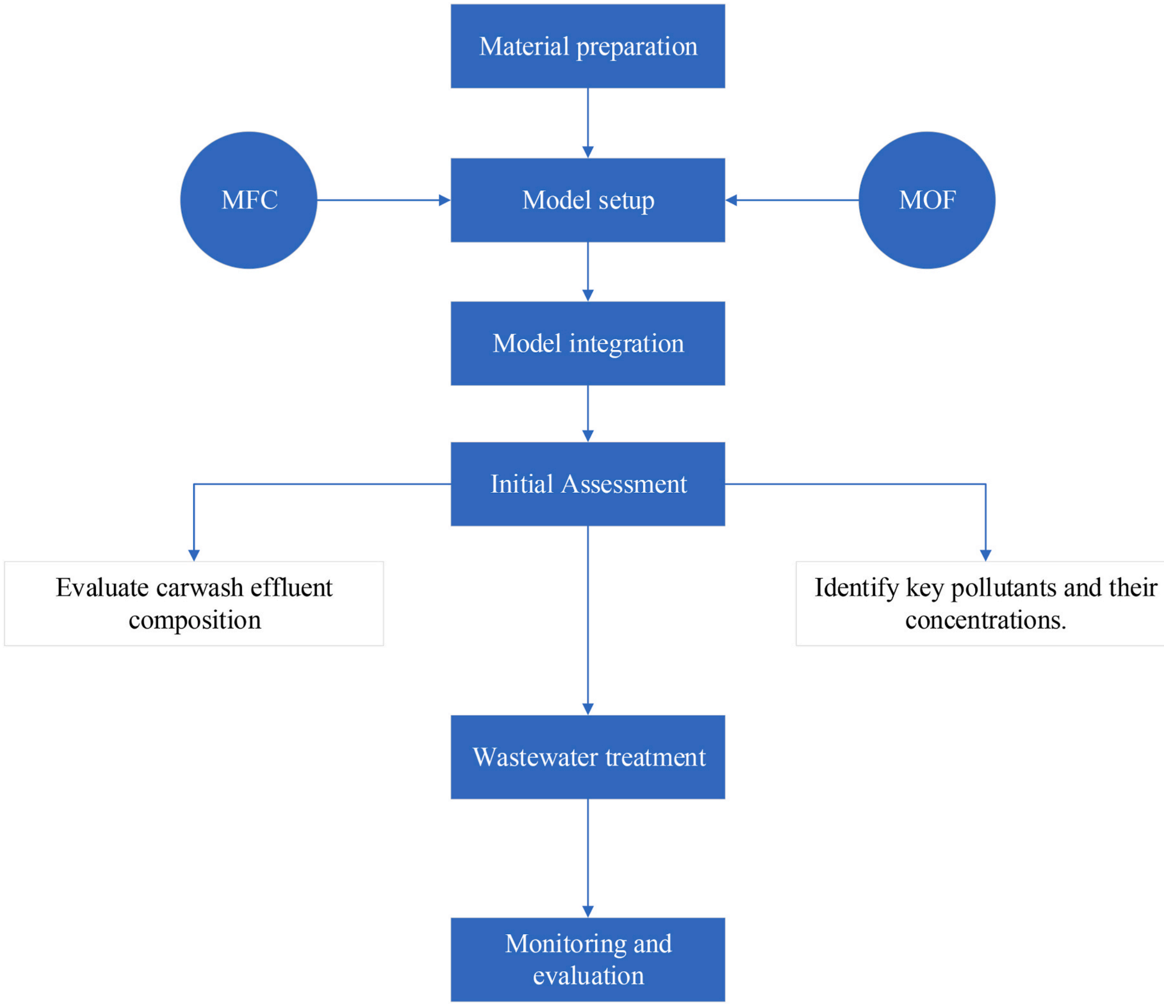


Fig. 3. The study step-by-step process flowchart.

Table 1
Weights and relative proportions given to the examined water quality parameters.

Parameter	Weight	Relative weight
Zinc	3	0.025
Total hardness	2	0.017
Calcium	2	0.017
Manganese	4	0.033
Fluorides	7	0.058
Nickel	3	0.025
Cadmium	8	0.067
Nitrates	7	0.058
Cyanides	8	0.067
Lead	9	0.075
Arsenic	10	0.083
TSS	2	0.017
TDS	2	0.017
TN	4	0.033
NH3–N	5	0.042
TP	4	0.033
FOG	6	0.050
EC	2	0.017
Cu	6	0.050
Surfactants	5	0.042
Turbidity	3	0.025
COD	7	0.058
BOD	6	0.050
TOC	5	0.042

consideration, 'R_W' for the determined relative weight, and 'g_i' for the weight assigned to each individual parameter. The computation of a quality rating scale (R_s) for each selected water quality parameter was another essential step. This was achieved by applying globally recognized standards to the division of each parameter's concentration by the corresponding recommended guideline value, and then multiplying the result by 100 [19,20] (Equation (4)).

$$R_s = \frac{t_i}{d_i} \times 100 \qquad \text{(Equation 4)}$$

Whereby; the concentration associated with each individual parameter is represented by the letter t_i, and the reference standard is represented by the symbol d_i for each measurement iteration.

Moreover, one of the most important steps in the process of developing the aggregated WQI was determining the sub-index (SI_i) for each individual water quality parameter. This process is explicitly described in Equation (5) [19,20].

$$SI_i = R_w \times R_s \qquad \text{(Equation 5)}$$

Ultimately, the total of all the sub-indices that were derived from the evaluation of every parameter that was investigated was used to develop the all-inclusive WQI [19,20] (Equation (6)).

$$WQI = \sum_{i=1}^{n} SI_i \qquad \text{(Equation 6)}$$

The WQI scores were grouped into distinct water condition categories, which included "exceptional water," "high-quality water," "substandard water," "extremely substandard water," and "water not suitable for consumption" [21,22]. The delineations for water quality categories were as follows: "exceptional water" for scores below 50, "high-quality" for scores falling between 50 and 100, "substandard" for scores ranging from 100 to 200, "extremely substandard" for scores spanning 200 to 300, and "unsuitable for drinking" for scores exceeding 300.

2.9. Cost analysis

The thorough cost analysis part of the study examined the financial complexities of upscaling the wastewater treatment system that incorporated MFC and MOF technologies. The analysis commenced by analyzing the equipment costs, which included the costs associated with acquiring and setting up MFC and MOF units in addition to any required infrastructure modifications. Moving on to operating expenses, the research explored the costs associated with electricity and maintenance that were incurred when the system was in operation. It also carefully examined the expenses associated with waste disposal, labor for maintenance and monitoring, and the chemicals used in the MOF process. The total cost of operation (CTotal), which was the sum of all these cost elements, provided a comprehensive picture of the associated financial outlay. The primary goal of this part of the study was to determine the net cost (CNet) after deducting income and savings. In addition, scaling-up options such as resource recovery (RRecovery) and possible energy efficiency savings (ESavings) were examined. This cost study was a useful tool for figuring out whether scaling up an MFC-MOF wastewater treatment system was economically feasible. In general, the cost analysis was conducted using United States Dollars (USD).

2.9.1. Equipment costs

Cost of MFC Units (CMFC): This includes the price of purchasing and setting up larger MFC units. Equation (7) provides a summary of the methodology used to calculate the MFC unit costs.

$$\text{MFC} = \text{Cost per unit} \times \text{Number of units} \quad \text{(Equation 7)}$$

Cost of MOF units (CMOF): This relates to the price of buying and setting up bigger MOF units for adsorption during the treatment procedure. Equation (8) summarises the methodology for estimating MOF unit costs.

$$\text{CMOF} = \text{Cost per unit} \times \text{Number of units} \quad \text{(Equation 8)}$$

Infrastructure Modification Costs (CIM): Costs associated with modifying existing infrastructure or constructing new facilities to accommodate the expanded system.

2.9.2. Operational costs electricity costs (CElectricity)

This may be computed using the power consumption and electricity rates, and it shows the cost of electricity used by the MFC-MOF system. Equation (9) is used for the computation.

$$\text{CElectricity} = \text{Power consumption (kW)} \times \text{Hours of operation} \times \text{Electricity rate (\$ / kWh)} \quad \text{(Equation 9)}$$

Maintenance costs (CMaintenance): These are the costs associated with labour and materials used for the routine maintenance of MFC and MOF units (Equation (10)).

$$\text{CMaintenance} = \text{Labor cost} + \text{Materials cost} \quad \text{(Equation 10)}$$

2.9.3. Chemical costs chemical costs for MOF (CChemicalMOF)

These expenses are related to the chemicals utilised in the MOF adsorption procedure; these include the price of the adsorbent materials and any other chemicals that may be required. Equation (11) can be used to explain the computation.

$$\text{CChemicalMOF} = \text{Cost of adsorbent materials} + \text{Cost of additional chemicals} \quad \text{(Equation 11)}$$

2.9.4. Labor costs (CLabor): these include labour costs for data collecting, maintenance, and monitoring, as well as salary and benefits for staff members who work on the system. Equation (12) can be used to express the calculation

$$\text{CLabor} = \text{Salary} + \text{Benefits} \quad \text{(Equation 12)}$$

2.9.5. Waste disposal costs waste disposal costs (CWasteDisposal)

This covers the price of getting rid of waste that is produced during the treatment procedure, like leftover chemicals or waste materials. Equation (13) provides an overview of the computation.

$$\text{CWasteDisposal} = \text{Cost of waste disposal} \quad \text{(Equation 13)}$$

2.9.6. Total cost of operation

The total cost of operation (CTotal), which is the total of all the expenses listed above, is crucial in figuring out how much it will cost to run the upgraded MFC-MOF system. Equation (14) is used to express the CTotal computation.

$$\text{CTotal} = \text{CMFC} + \text{CMOF} + \text{CIM} + \text{CElectricity} + \text{CMaintenance} + \text{CChemicalMOF} + \text{CLabor} + \text{CWasteDisposal} \quad \text{(Equation 14)}$$

2.10. Strategies for scaling up

2.10.1. Savings on energy efficiency (ESavings)

Quantifying the possible decrease in power costs by integrating energy-efficient parts and practises is known as energy efficiency savings, or ESavings. Equation (15) can be used to calculate ESavings by subtracting the present electricity costs (CElectricity) related to the current system from the electricity expenses (CElectricity) incurred under an optimized system.

$$\text{ESavings} = \text{CElectricity (current system)} - \text{CElectricity (optimized system)} \quad \text{(Equation 15)}$$

2.10.2. Resource recovery potential (RRecovery)

Potential revenue from resource recovery, such as valuable byproducts or treated water for non-potable uses, is evaluated to determine resource recovery potential, or RRecovery. Equation (16) defines recovery as the amount obtained by deducting the resource recovery costs from the revenue produced by the recovered resources.

$$\text{RRecovery} = \text{Revenue from recovered resources} - \text{Costs associated with recovery} \quad \text{(Equation 16)}$$

2.10.3. Net cost (CNet)

After taking into account both cost reductions and revenue components, the final cost number is evaluated to determine the net cost (CNet). After subtracting the energy efficiency savings (ESavings) from the overall cost (CTotal), add the revenue from resource recovery (RRecovery) to arrive at CNet (Equation (17)).

$$CNet = CTotal - ESavings + RRecovery \quad \text{(Equation 17)}$$

2.11. The applied statistical methods

2.11.1. Analysis of variance

To identify statistically significant differences in the complex matrix of water quality data, single-factor analysis of variance (ANOVA) was utilised as a stactical technique in this investigation. It is crucial to emphasize that this analytical approach carefully assesses the degree of divergence inherent in each cluster of water quality data selected from each individual cohort. The statistical significance was assessed by comparing the calculated p-values to the predetermined alpha threshold, which was initially set at 0.05. It is important to note that the alpha number represents the likelihood that the null hypothesis will be rejected in the future, even in cases where it remains true. The veracity of the null hypothesis subsists in cases where the resultant p-value eclipses the stipulated alpha threshold. Speaking to the nuanced role of the p-value, it serves as an exquisite indicator of the likelihood of attaining an outcome more exceptionally divergent from the outcomes of the experimental venture [23–25].

2.11.2. Correlation analysis

In addition, the study attempted to investigate possible correlations between different metrics of water quality in order to determine the degree to which one parameter could function as a trustworthy indication or have an impact on another. The study also explored the complex relationships among many factors and how those relationships affect the overall performance of the systems that are being studied. The following is the scale that shows how strongly the variables are related to one

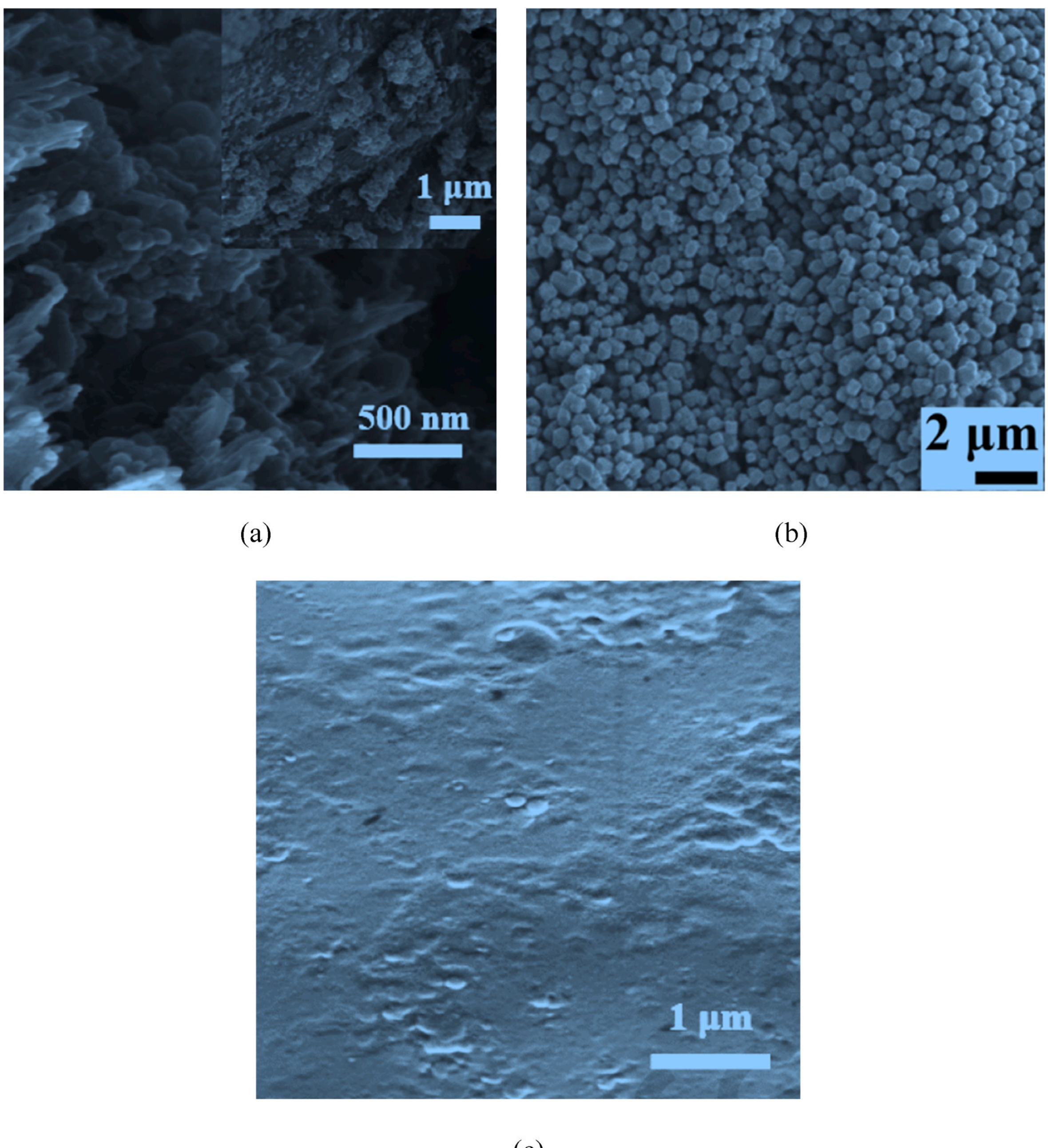


Fig. 4. Morphological characteristics of the material (a) composite material (b) Zeolitic Imidazolate Framework-8 (c) Polyethersulfone.

another: A relationship is considered low if it falls between 0 and 0.29, moderate if it falls between 0.3 and 0.49, significant if it falls between 0.5 and 0.69, and large if it falls between 0.7 and 1.

3. Results and discussion

3.1. Material characterization

The synthesised materials were subjected to a thorough SEM study, which offered a thorough examination of the surface and structural properties of several constituents, including the polymeric composite beads and pure Zeolitic Imidazolate Framework-8 particles (Fig. 4). The internal and surface properties of these components have been shown in great detail by the SEM imaging. A fascinating textural-like pattern is revealed upon close inspection of the Polyethersulfone bead's cross-sectional image, highlighting the existence of easily visible macropores inside the internal structure of the bead. The Polyethersulfone bead's surface is particularly noteworthy since it seems remarkably homogeneous and smooth, with no visible particles or imperfections. The Polyethersulfone material's purity and integrity are indicated by its polished surface. On the other hand, the SEM pictures provide a clear depiction of an amazing thing that's happening inside the polymeric composite beads. Not only are zeolitic imidazolate framework-8 particles clearly visible, but they are also carefully distributed and skillfully coated onto the surface of these beads. This intriguing finding reveals a notable movement of Metal-Organic Framework (MOF) particles from the composite material's inner to exterior. There are obvious changes to the polymeric composite's surface as a result of this migration. These changes show themselves as the formation of noticeable depressions and elevated areas. These surface imperfections provide important information about the dynamic interplay between the integrated MOF particles and the polymeric matrix, illuminating the distinct structural properties of the resultant composite material.

3.2. Raw wastewater characterization

3.2.1. General characterization

Table 2 provides an extensive summary of the parameters that characterise raw effluent from carwashes. Understanding the quality and content of wastewater is crucial, and observing changes in these characteristics can shed light on possible sources and the overall impact on the ecosystem. From the results, it can be seen that zinc has a mean content of 6.17 mg/L and varies from 2.30 mg/L to 9.10 mg/L. This indicates that a considerable variety of zinc, which might come from many sources including tyres, car parts, or road runoff, is present in the wastewater. There is a noticeable range in total hardness from 103.30 mg/L to 371.10 mg/L, which suggests that water hardness varies during the carwash processes. The range of TSS concentrations (452.50–683.60 mg/L) indicates the presence of solid particles in the wastewater. TDS ranges more widely, from 874.50 mg/L to 1431.20 mg/L, suggesting a variety of dissolved materials. These results highlight the complexity of the dissolved and particulate matter in the wastewater. Additionally, moderate changes are seen in indices like COD, BOD, and TOC, indicating the presence of both organic and inorganic elements that contribute to the overall pollution load. All in all, these findings demonstrate the dynamic character of wastewater from vehicle washes, with different levels of organic components, sediments, and heavy metals. This kind of data is crucial for creating treatment plans that work and for dealing with environmental issues. These results also emphasize the importance of monitoring and managing carwash wastewater to mitigate its potential impact on water quality and ecosystems. In the literature, it has been observed that carwash wastewater is noted as one of the most heavily contaminated types of wastewater, characterized by a high level of impurities [26]. The research carried out by Hashim and Zayadi [27] found comparable elevated concentrations of TSS and COD in carwash wastewater.

Table 2
Characteristics of the raw wastewater based on the 25 investigated water quality parameters.

Parameter	Min	Max	Mean	Median	STD
Zinc	2.30	9.10	6.17	6.50	2.34
Total hardness	103.30	371.10	251.57	288.10	96.18
Calcium	74.40	267.60	174.55	190.50	73.00
Manganese	0.26	0.49	0.36	0.35	0.08
Fluorides	1.40	3.80	2.72	2.85	0.76
Nickel	2.48	8.61	4.95	4.49	1.93
Cadmium	0.00	0.02	0.01	0.01	0.01
Nitrates	23.80	49.20	35.00	34.70	9.13
Cyanides	0.00	0.20	0.07	0.05	0.07
Lead	0.01	0.09	0.03	0.02	0.03
Arsenic	0.00	0.00	0.00	0.00	0.00
TSS	452.50	683.60	549.40	543.05	83.43
TDS	874.50	1431.20	1143.63	1146.20	218.68
TN	43.30	63.40	53.87	54.40	6.27
NH_3–N	30.20	42.20	37.45	39.00	3.90
TP	12.50	20.50	17.30	17.95	2.68
FOG	68.80	193.30	149.23	158.30	43.29
EC	816.90	1468.80	1130.18	1182.20	229.80
Cu	0.40	0.84	0.58	0.58	0.14
Surfactants	16.60	44.30	29.95	30.80	10.87
Turbidity	114.80	289.40	185.80	184.60	59.52
COD	265.20	382.50	305.15	285.75	42.84
BOD	51.20	99.30	78.23	80.35	18.43
TOC	48.40	88.50	72.63	79.05	14.58

Patterns in the distribution of different water quality parameters can be seen in the boxplots displayed in Fig. 5. The median lines for TSS, TDS, FOG, BOD, zinc, nitrates, cyanides, and TSS are placed towards the centre of the boxplots, suggesting a normally distributed or statistically symmetric dataset. The median lines for COD and nickel, on the other hand, are closer to the lower region of the boxplots, suggesting a statistically favourably skewed distribution of the data. On the other hand, the median line is significantly closer to the upper portion of the boxplot for total hardness, calcium, fluorides, TN, NH3–N, TP, EC, copper, turbidity, and TOC, indicating a statistically negatively skewed data distribution.

3.2.2. Correlation analysis

A correlation matrix reflecting the correlations between several characteristics in the carwash raw wastewater is shown in Table 3. This matrix clarifies the intricacies of the wastewater composition by offering insightful information on the relationships between various contaminants and water quality indicators. Beginning with hydrocarbons, or oils and grease, it has a robust positive connection with multiple metrics, most notably TOC (0.9690) and turbidity (0.9674). These strong connections imply that hydrocarbons are more prevalent in wastewater as turbidity levels and TOC concentrations grow. Given that turbidity often arises from solid particles, this correlation hints at the potential presence of suspended hydrocarbons [28]. The close relationship with TOC highlights how susceptible TOC is to many contaminants. TSS shows favourable associations with turbidity (0.6048), oils/grease (0.3908), and surfactants (0.7448). These results suggest that there is a small relationship between increased levels of turbidity, hydrocarbons, and surfactants and TSS concentrations. This suggests that the presence of hydrocarbons and surfactants in the wastewater may be associated with solid particles, maybe resulting from runoff from car washes. The chemicals called surfactants, which are added to carwash procedures specifically to improve cleaning, show a substantial positive link with a number of measures, such as oils/grease (0.7148), TSS (0.7448), and turbidity (0.7882). This underlines the connection between surfactants and the presence of hydrocarbons, solid particles, and turbidity in the wastewater. Overall, the correlation matrix highlights intricate relationships among parameters, revealing how various pollutants and water quality indicators within the carwash raw wastewater are interconnected [29]. These insights are critical for understanding the

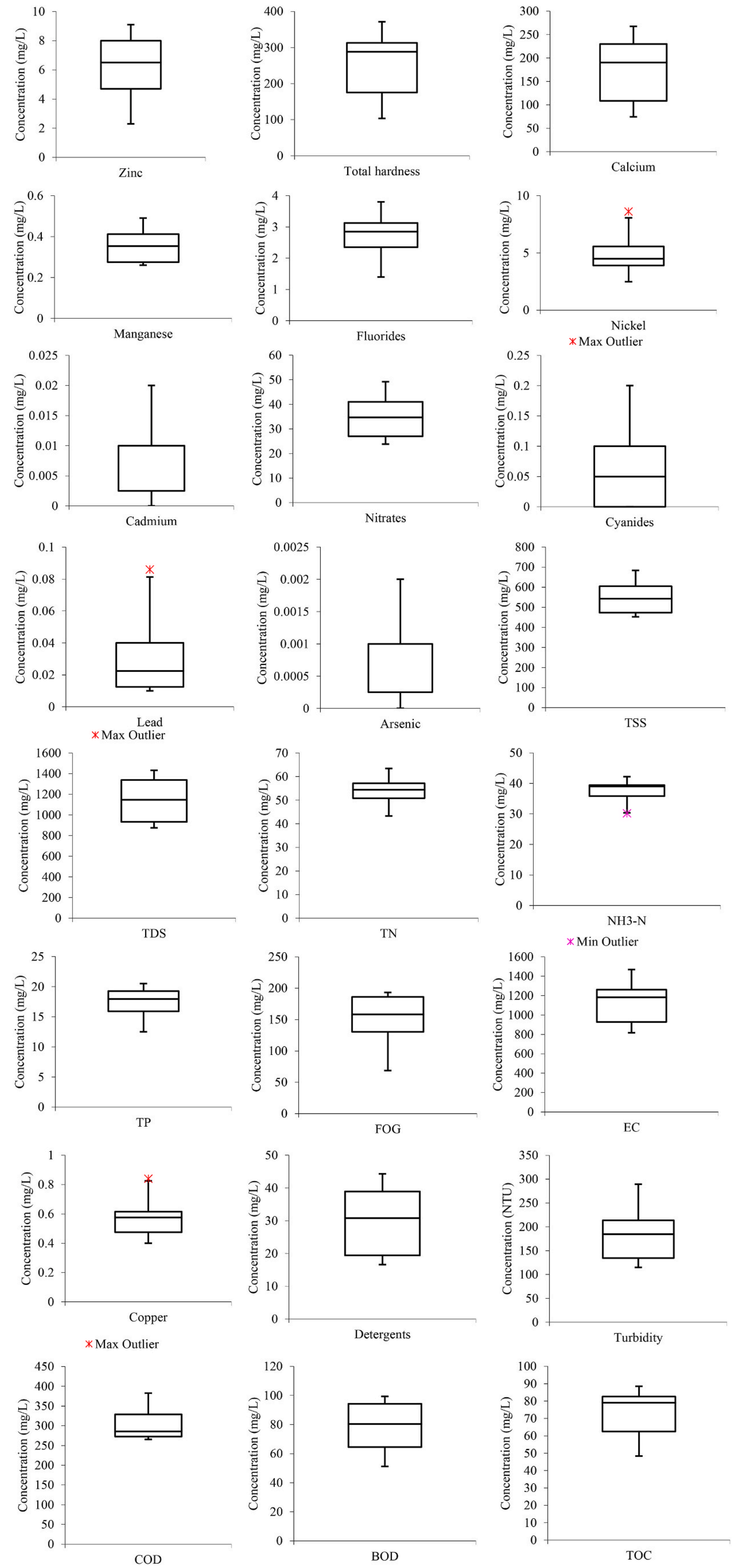
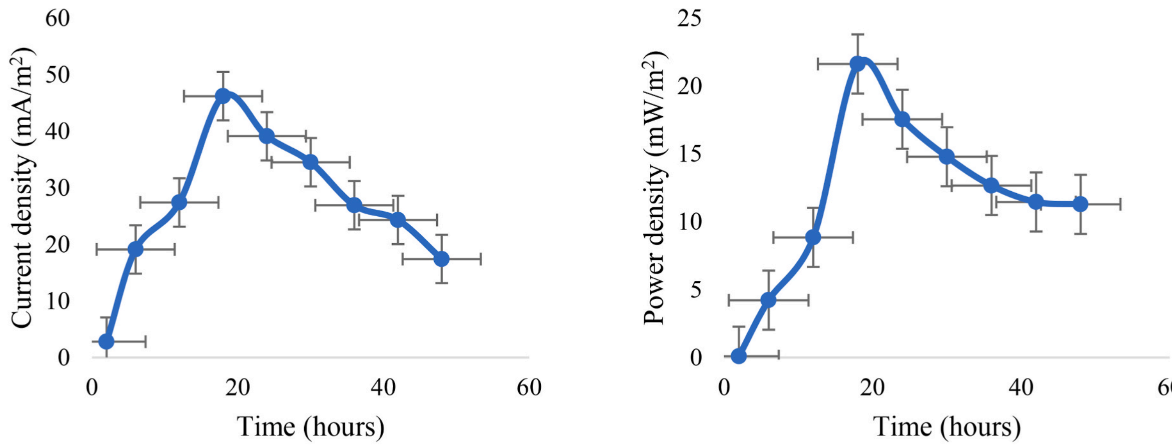


Fig. 5. Data distribution analysis using boxplots.

Table 3
The correlation matrix table from the raw wastewater concentration results.

	Oils/Grease	TSS	Surfactants	Turbidity	TDS	COD	BOD	TOC	TP
Oils/Grease	1								
TSS	0.3908	1							
Surfactants	0.7148	0.7448	1						
Turbidity	0.9674	0.6048	0.7882	1					
TDS	0.6643	0.6650	0.8942	0.7222	1				
COD	0.4499	0.6723	0.8765	0.5394	0.5929	1			
BOD	0.6545	0.4874	0.8349	0.6603	0.9760	0.5122	1		
TOC	0.9690	0.5072	0.8047	0.9691	0.6576	0.6367	0.6173	1	
TP	0.7075	0.7102	0.9479	0.7800	0.7088	0.9472	0.6300	0.8459	1



(a) (b)

Fig. 6. Microbial performance analysis (a) current density (b) power density.

wastewater composition and the potential sources of contamination, thereby guiding the development of appropriate treatment strategies and pollution control measures.

The time-dependent study shows the current and power densities' temporal evolution in the MFC treatment system (Fig. 6). The data shows that there is a minimal power density of 0.095 mW/m^2 and a relatively low current density of 2.8 mA/m^2 over the first 2 h. The experiment's current and power densities, however, show a notable

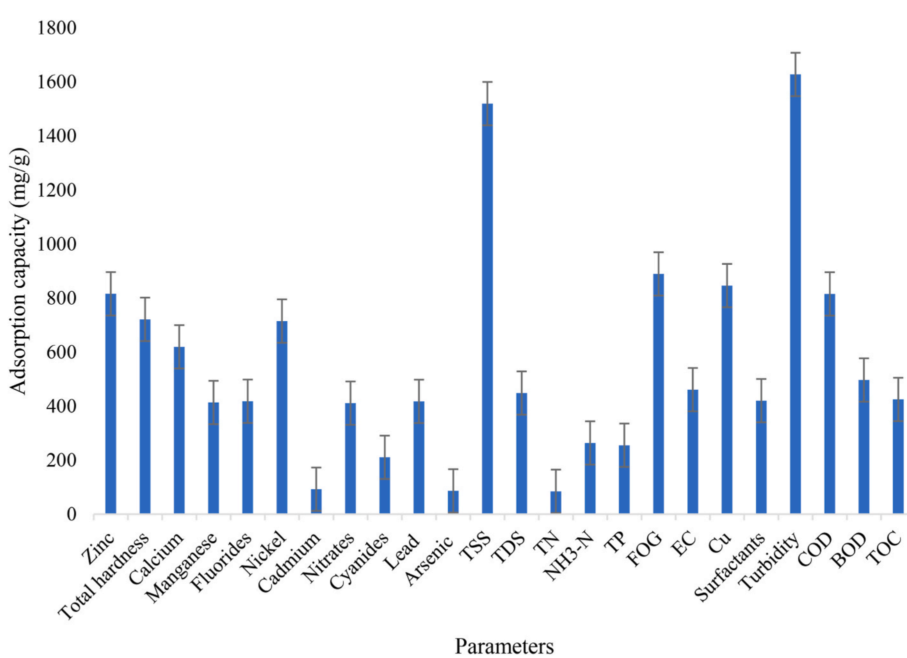


Fig. 7. Adsorption capacities from different parameters.

increase as it goes on, culminating at 46.2 mA/m^2 and 21.62 mW/m^2, respectively, at the 18-h point. Then, current density gradually drops while power density stays reasonably high, indicating that microbial activity may have stabilised or even slightly decreased. The system maintains a current density of 17.4 mA/m^2 and a power density of 11.28 mW/m^2 at the conclusion of the 48-h experiment. These results demonstrate the potential of the MFC treatment system for continuous energy production from organic matter degradation. During the course of the experiment, there was an initial period of significant performance improvement, followed by a relatively stable yet efficient phase in electricity generation.

3.3. Adsorption capacity

The outcomes show that the integrated MOF has a remarkable adsorption capability for a variety of parameters in the treatment of

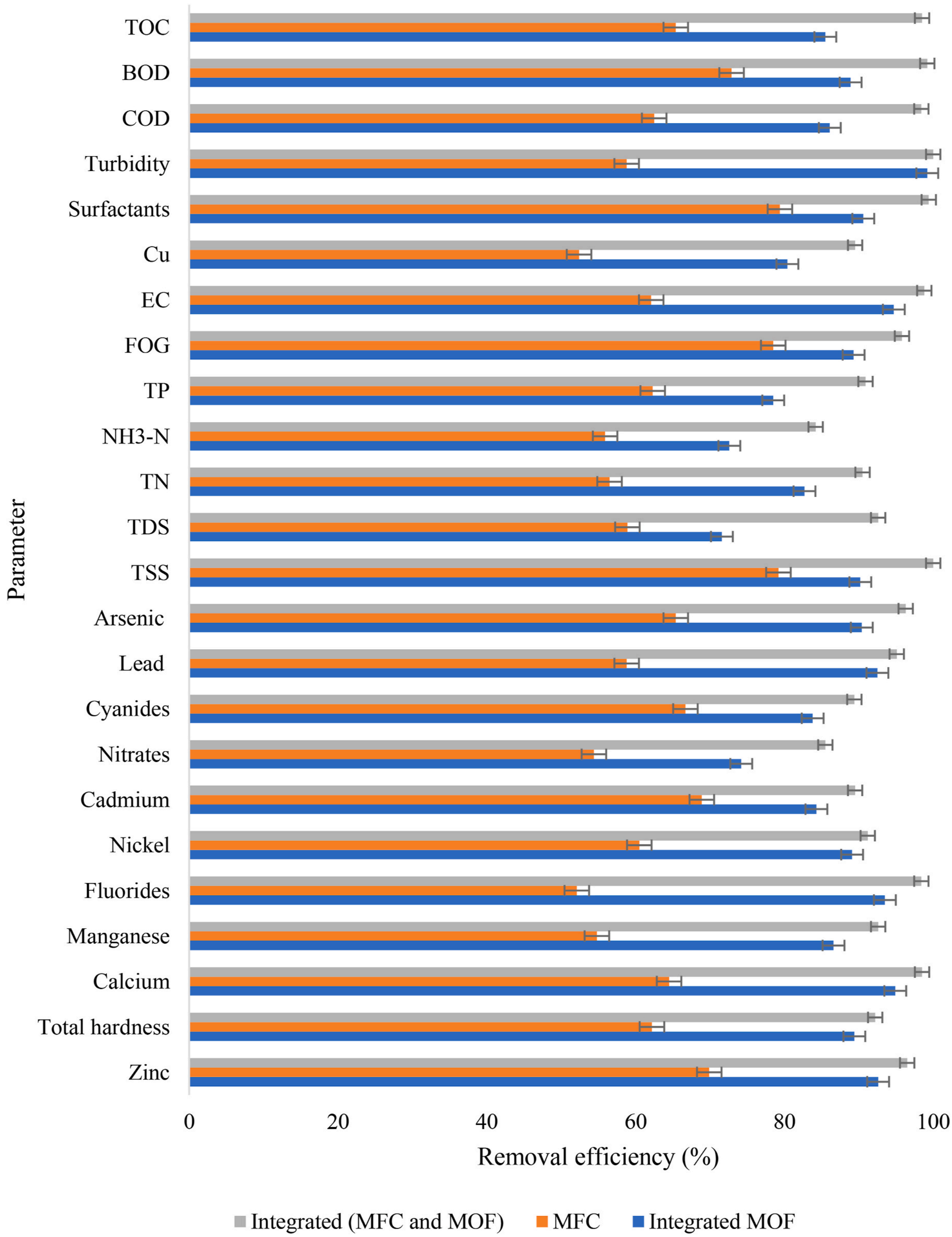


Fig. 8. Removal efficiencies from different parameters.

carwash effluent (Fig. 7). Zinc stands out among heavy metals with a notable adsorption capacity of 815.7 mg/g, followed by Nickel and Copper. Significant adsorption capacities are also demonstrated by water quality indicators like calcium and total hardness, which have respective values of 619.8 mg/g and 721.3 mg/g. Furthermore, contaminants with considerable adsorption capabilities include manganese, fluorides, and nitrates. As demonstrated by its excellent adsorption capabilities for TSS, FOG, COD, BOD, and TOC, the MOF efficiently eliminates organic materials. This effectively reduces turbidity, a typical problem in carwash wastewater, with an adsorption capacity of 1628 mg/g. These results underscore the exceptional potential of integrated MOF in enhancing water quality and reducing pollution in carwash wastewater treatment. In the study carried out by Gaikwad et al. [30], similar findings were documented, with an adsorption capacity of up to 511 mg/g achieved for benzene when MOF-199 was uased. It is worth highlighting that owing to their attractive attributes, including a substantial surface area, porous structure, and robust chemical and solvent resistance, MOFs have been under investigation for the removal of hazardous substances from wastewater. Nevertheless, to enable the widespread adoption of MOFs for the extraction of toxic materials, certain challenges, such as the need for a more straightforward separable design, must be overcome. For instance, in a study by Ahmed et al. [31], they employed ultrasonication to synthesize Iron(II,III) oxide@University of Oslo-66-NH_2 for the removal of Cd^{2+} and Pb^{2+} from an aqueous solution. This approach resulted in an impressive maximum adsorption capacity of 714.3 mg/g for Cd^{2+} and 833.3 mg/g for Pb^{2+}, while also demonstrating excellent reusability. Furthermore, in addition to the findings regarding the composite MOF's performance in our study, Lopez-Cervantes et al. [32], conducted research on the application of biosorbent chitosan–glutaraldehyde derived from shrimp shells. They explored its efficacy in removing the textile dye Direct Blue 71 from an aqueous solution and observed an impressive adsorption capacity of up to 343.59 mg/g for dye removal.

3.4. Removal efficiency

When compared to individual treatment approaches, the integrated MOF and MFC treatment combination results for different parameters demonstrate promising higher removal efficiency (Fig. 8). When it comes to eliminating various contaminants from wastewater, the combination of MOF and MFC seems to work well together. Higher removal efficiencies are consistently shown by integrated treatment with MOF and MFC in the first set of parameters, which includes heavy metals including zinc, nickel, and cadmium. For instance, when MOF and MFC are combined, zinc removal efficiency rises from 92.6 % with integrated MOF to 96.5 %. The MFC enhances the effectiveness of MOF's heavy metal removal process and makes a major contribution to the removal of organic contaminants. The combo of MOF and MFC also performs admirably in the second set of criteria, which includes organic pollutants like BOD and TOC. With the integrated strategy, the removal efficiency of BOD rises from 88.9 % with MOF to 99.2 %. The MFC's microbial activity aids in the organic matter's biodegradation, which facilitates improved removal. EC, TSS, and turbidity are examples of general water quality indicators that are included in the third group of parameters. Nevertheless, it's crucial to acknowledge that the utilization of Microbial Fuel Cells (MFC) for wastewater treatment and potential electricity generation is not free from challenges. As outlined by Shabani et al. [33], the authors emphasized that the MFC field is advancing, supported by a multitude of well-established methods and ongoing research. A primary concern in the prospective implementation of a dual-chamber MFC involves achieving the optimal separation of the two compartments. Outstanding removal efficiencies are demonstrated by integrated MOF and MFC treatment, with 100 % removal of turbidity and TSS. Water clarity is enhanced and fine suspended particle removal is significantly aided by the MFC. Overall, the findings show that the combination of MOF and MFC offers a great deal of potential for thorough wastewater treatment because it can efficiently remove a variety of pollutants, including organic compounds, heavy metals, and general indicators of water quality. To fully realise the promise of this integrated method in practical applications, more study and proper system optimization are needed. In scholarly works, it is recognized that combining various treatment methods for wastewater treatment holds the potential to notably enhance system performance. Meiramkulova et al. [34], for example, observed that the diversity of pollutants in wastewater poses challenges to achieving high removal efficiency using a single treatment unit. They demonstrated this by achieving almost 100 % removal efficiency for total suspended solids in poultry slaughterhouse wastewater when integrating electrochemical methods with membration filtration techniques.

3.5. Analysis of variance

Findings from the ANOVA indicate that at least two of the groups differ significantly from one another (Table 4). The p-value (7.88×10^{-24}) is low, well below the usual significance level of 0.05, supporting this. Furthermore, demonstrating the substantial disparities between the groups, the "Between Groups" variation (6896.924) is significantly larger than the "Within Groups" variation (56.632). A 0.05 significance level places the F-statistic (121.7839) much above the crucial F-value (3.124). All things considered, the findings imply that there is a significant difference between at least one of the groups, if not more. Additional studies or post-hoc tests could be necessary to identify whether particular groups are different, though. The analysis of variance is crucial in research as it enables the identification and quantification of the sources of variation in data, allowing researchers to assess the significance of differences between groups and draw meaningful conclusions from experimental or observational studies [35].

3.5.1. Based on ANOVA

3.6. Water quality analysis based on WQI

The results in Table 5 display the WQI computations for various water quality parameters in different treatment stages, including raw wastewater, MFC, composite MOF, and integrated treatment. The "qi" values represent the quality ratings for each parameter, while "sli" represents the corresponding sub-indices. Notably, the "qi" values decrease as water treatment progresses from raw wastewater to the Integrated stage, indicating an improvement in water quality. Parameters such as manganese, nickel, and turbidity exhibit higher "qi" values in the raw wastewater but significantly decrease in the Integrated treatment, reflecting substantial reductions in contamination. Conversely, some parameters like total hardness and calcium have consistently low

Table 4
Summary of the ANOVA results from the raw wastewater and treated effluents.

Groups	Count	Sum	Average	Variance		
Integrated MOF	25	2161.2	86.448	51.616		
MFC	25	1557.4	62.296	96.278		
Integrated (MOF + MFC)	25	2353.1	94.124	22.004		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	13793.85	2	6896.924	121.7839	7.88×10^{-24}	3.124
Within Groups	4077.538	72	56.632			
Total	17871.38	74				

Table 5
Summary of the WQI computations.

Parameter	Raw wastewater		MFC		Composite MOF		Integrated	
	qi	sli	qi	sli	qi	sli	qi	sli
Zinc	123.333	3.083	37.123	0.928	9.127	0.228	4.317	0.108
Total hardness	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Calcium	349.100	5.818	123.931	2.066	17.804	0.297	5.236	0.087
Manganese	712.333	23.744	321.975	10.732	95.453	3.182	52.713	1.757
Fluorides	67.917	3.962	32.532	1.898	4.415	0.258	1.087	0.063
Nickel	4950.333	123.758	1955.382	48.885	539.586	13.490	435.629	10.891
Cadmium	166.667	11.111	51.833	3.456	26.167	1.744	17.500	1.167
Nitrates	350.000	20.417	159.600	9.310	90.300	5.268	50.750	2.960
Cyanides	33.333	2.222	11.100	0.740	5.400	0.360	3.533	0.236
Lead	217.778	16.333	89.724	6.729	16.333	1.225	10.671	0.800
Arsenic	8.333	0.694	2.883	0.240	0.800	0.067	0.308	0.026
TSS	5494.000	91.567	1142.752	19.046	538.412	8.974	0.000	0.000
TDS	228.727	3.812	94.007	1.567	64.958	1.083	16.926	0.282
TN	538.667	17.956	234.320	7.811	93.189	3.106	51.173	1.706
NH3–N	3745.000	156.042	1651.545	68.814	1026.130	42.755	295.855	12.327
TP	17300.000	576.667	6522.100	217.403	3719.500	123.983	1574.300	52.477
FOG	149.233	7.462	32.085	1.604	15.968	0.798	6.268	0.313
EC	452.073	7.535	171.336	2.856	23.960	0.399	5.425	0.090
Cu	44.359	2.218	21.115	1.056	8.694	0.435	4.658	0.233
Surfactants	5990.000	249.583	1233.940	51.414	563.060	23.461	35.940	1.497
Turbidity	61933.333	1548.333	25516.533	637.913	495.467	12.387	0.000	0.000
COD	6103.000	356.008	2288.625	133.503	848.317	49.485	97.648	5.696
BOD	2607.778	130.389	706.708	35.335	289.463	14.473	20.862	1.043
TOC	1452.667	60.528	502.623	20.943	210.637	8.777	21.790	0.908

"qi" values across all treatment stages, indicating minimal variation. These results underscore the effectiveness of the treatment processes in enhancing water quality, with the Integrated treatment stage achieving the lowest "qi" values, indicating the highest water quality. To provide further detail, the data highlights that turbidity had the greatest impact on the quality rating and sub-index, registering values of 61933.333 and 1548.333, respectively. This suggests that the carwash wastewater exhibited significant pollution specifically in terms of turbidity, surpassing recommended guidelines. Remarkably, following the integrated treatment, both the quality rating and sub-index show a value of 0, underscoring the substantial effectiveness of the integrated approach in wastewater treatment. As stated by Al-Gheethi et al. [26], the elevated turbidity level can be attributed to the existence of dirt, mud, and brake particles in the wastewater, originating from vehicles and characterized by relatively large molecule sizes.

The results in Table 6 provide an overview of the aggregated Water Quality Index (WQI) values for different water sources, accompanied by their respective definitions. The WQI values serve as a comprehensive assessment of water quality, with higher values indicating poorer quality. In this context, the raw water source demonstrates an exceptionally high WQI of 3419.243, categorizing it as "Unsuitable for drinking," signifying significant contamination and safety concerns. As water undergoes treatment stages, such as Modified Fenton's Coagulation (MFC) and Composite Modified Fenton's (MOF), the WQI values progressively decrease, but they still fall under the "Unsuitable for drinking" classification. The Integrated treatment stage stands out with a significantly lower WQI of 94.668, classifying the water as "Standard or good water," indicating its suitability for drinking and standard usage. These results underscore the substantial improvement in water quality through the treatment process, with the Integrated stage achieving the desired quality standards for potable water. It is also important to note that, the use of water quality indices is crucial for water quality analysis as it provides a comprehensive and easily interpretable assessment of multiple water parameters, facilitating effective monitoring and management of water resources [36].

Table 6
Summary of the aggregated WQIs.

Water source	WQI	Definition
Raw	3419.243	Unsuitable for drinking
MFC	1284.249	Unsuitable for drinking
Composite MOF	316.233	Unsuitable for drinking
Integrated (MFC + MOF)	94.668	Standard or good water

Table 7
Summary of the cost analysis.

Cost Component	Calculation	Typical monthly Cost (USD)
Equipment Costs	CMFC + CMOF + CIM	$25,000
Operational Costs	CElectricity + CMaintenance + CChemicalMOF + CWasteDisposal	$8000
Labor Costs	CLabor	$5000
Total Annual Cost of Operation	**Total of Equipment, Operational, and Labor Costs**	**$38,000**
Energy Efficiency Savings	CElectricity (Current System) - CElectricity (Optimized System)	$1500
Resource Recovery Potential	Revenue from recovered resources - Costs associated with recovery	$2000
Net Annual Cost	**CTotal - ESavings + RRecovery**	**$34,500**

3.7. Cost analysis

Particularly when contrasted with alternative treatment techniques, the cost analysis results for the MFC-MOF system in carwash wastewater treatment have important ramifications (Table 7). The MFC-MOF system's $38,000 monthly cost highlights the necessary financial commitment for efficient operation. In comparison to traditional treatment techniques like activated sludge systems, the MFC-MOF system could be more expensive. Nonetheless, there are a number of benefits to the MFC-MOF system that should be taken into account. In contrast, conventional treatment techniques frequently result in increased waste material disposal expenses and do not offer the same potential for resource recovery as the MFC-MOF system. The MFC-MOF system's novel approach to wastewater treatment indicates its potential to be both economically and environmentally sustainable, even though the initial investment may be more. When assessing the economic ramifications, it is critical to balance the short-term expenses with the long-term profits and take prospective savings and revenue production into account. In conclusion, the MFC-MOF system is a promising development in wastewater treatment that differs from conventional treatment techniques by providing a balanced financial picture when taking into account both its expenses and prospective savings as well as resource recovery capabilities. As per Chan et al. [37], the discharge of pollutants into water streams and soil through industrial effluents has resulted in numerous detrimental impacts on the environment, health, and ecosystems. Over the past decades, there have been concerted endeavors by scientists to innovate and advance methods for removing pollutants from wastewater. Nonetheless, the conventional techniques employed for pollutants removal are expensive and carry the risk of causing secondary pollution, including contamination of soil and water bodies. This underscores the significance of exploring more economical treatment methods for wastewater treatment.

3.8. Cost comparative analysis

Table 8 presents a comparative analysis of estimated operating costs for various wastewater treatment plants, including those described in this study and those reported in various global locations. The data suggests that the anticipated running costs determined by this study are significantly more cost-effective when compared to the costs revealed for wastewater treatment plants worldwide. The cost-effectiveness and future viability of the recommended treatment approach described in this study are highlighted by this cost-efficiency. It means that the system developed in this study presents a cost-effective method of treating wastewater when compared to global norms, making it an attractive option for wastewater treatment.

It is crucial to emphasize that the economic aspect of treating carwash wastewater is a vital factor for balancing environmental sustainability and financial viability [38]. Conventional treatment approaches typically incur substantial costs, encompassing the setup and upkeep of intricate systems essential for efficient pollutant removal [7]. The expenses associated with energy consumption, chemicals, and specialized equipment can exert a notable influence on the overall operational budget of carwash wastewater treatment facilities. Consequently, there is an increasing demand to investigate and adopt more economically feasible and sustainable methods that align with environmental guidelines [39]. In recent years, there has been a heightened focus on the development of innovative and economically feasible technologies for wastewater treatment [40]. Advanced treatment processes, such as the integration MFC and MOF with Graphene Oxide, present promising alternatives. These technologies aim to enhance pollutant removal efficiency while addressing the economic constraints associated with conventional methods. By leveraging the synergistic effects of MFC, MOF, and Graphene Oxide, there is potential for achieving higher treatment efficiency at reduced operational costs, making the approach more economically viable for widespread adoption. Despite the potential benefits of advanced technologies, the economic feasibility of carwash wastewater treatment also relies on factors such as scalability, ease of implementation, and long-term operational costs [41]. Conducting a comprehensive cost-benefit analysis that considers both initial investment and ongoing operational expenses is essential. This approach ensures that the chosen wastewater treatment method not only meets environmental standards but is also economically sustainable for carwash facilities, promoting a balance between effective treatment and financial prudence.

Table 8
Comparative cost analysis.

Wastewater Treatment System	Key Factors Influencing Annual Costs	Annual Expenditure (USD)	Source
Integrated MFC and MOF System	Costs related to the purchase and installation of larger MFC and EF units, infrastructure modifications, electricity usage, maintenance, chemicals, labor, and waste disposal.	456,000	This study
Advanced Biological Treatment System	Expenses tied to electricity consumption, chemicals employed, staffing levels, and maintenance and repairs.	592,740	[42]
Conventional Activated Sludge System	Costs encompass operation, maintenance, materials, chemicals, and energy.	256,300	[43]
Conventional Activated Sludge with Pre-Denitrification	Expenses associated with operation, maintenance, materials, chemicals, and energy.	524,000	[43]
Membrane Bioreactor System	Annual costs include operation, maintenance, materials, chemicals, and energy.	1,040,000	[43]
Trickling Filtration System	Annual costs comprise operation, maintenance, materials, chemicals, and energy expenses.	2,465,520.77	[44]
Complete-Mix Activated Sludge System	Annual costs consist of operation, maintenance, materials, chemicals, and energy.	3,759,205.94	[44]
Oxidation Ditch Activated Sludge System	Annual costs involve operation, maintenance, materials, chemicals, and energy.	3,593,629.17	[44]

4. Conclusion

The study explored the synergistic potential of integrating MFC with MOF enhanced by graphene oxide for carwash effluent treatment. The research, structured into three main parts, systematically analyzed MFC, the composite MOF, and the combined MFC and MOF strategy. The results demonstrated a significant synergistic effect, especially in pollutant removal, with the simultaneous application of MOF and MFC surpassing individual treatment approaches. For heavy elements like zinc, nickel, and cadmium, the combined treatment consistently exhibited higher removal rates, exemplified by the outstanding 96.5 % removal of zinc, compared to 92.6 % with integrated MOF alone. Moreover, the integrated approach excelled in removing organic pollutants, achieving a remarkable 99.2 % removal of BOD. The microbial activity in MFC significantly contributed to enhancing the elimination of organic materials. In terms of general water quality parameters, the combined treatment showcased exceptional efficiency, completely removing turbidity and total suspended solids, achieving a 100 % removal rate. Moreover, the MFC exhibited a modest start with low power density (0.095 mW/m^2) and current density (2.8 mA/m^2) over the initial 2 hours. Subsequently, a notable surge occurred, reaching its peak at 46.2 mA/m^2 and 21.62 mW/m^2 by the 18th hour. Despite a subsequent decline in current density, the power density remained relatively high, suggesting a stabilization of microbial activity. The 48-h experiment concluded with a current density of 17.4 mA/m^2 and a power density of 11.28 mW/m^2. This trajectory underscores the dynamic behavior of the microbial fuel cell over the experimental period, indicating both adaptability and sustained efficiency in power generation. Despite the comparatively higher monthly cost of the MFC-MOF system, which stood at $38,000, the study highlighted its economic and environmental advantages, including resource recovery and lower disposal costs. This research signifies a promising development in wastewater treatment, offering a comprehensive solution for the elimination of diverse contaminants. While acknowledging the initial costs, the long-term benefits, both economically and environmentally, underscore the potential for practical applications in real-world scenarios. The study encourages further exploration, emphasizing ongoing research and system optimization to maximize the effectiveness and applicability of this integrated approach to address wastewater treatment challenges.

Data accessibility statement

The data that contributed to the findings and conclusions of this study are available upon reasonable request from the authors.

CRediT authorship contribution statement

Timoth Mkilima: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yerkebulan Zharkenov:** Project administration, Funding acquisition, Formal analysis, Data curation. **Laura Utepbergenova:** Validation, Resources, Data curation. **Elmira Smagulova:** Validation, Resources, Data curation. **Kamidulla Fazylov:** Resources, Investigation, Data curation. **Iliyas Zhumadilov:** Visualization, Resources, Investigation, Data curation. **Kamilya Kirgizbayeva:** Resources, Investigation, Data curation. **Aizhan Baketova:** Resources, Data curation. **Gulnara Abdukalikova:** Data curation, Investigation, Resources.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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