Optimization of micropollutant removal from wastewaters using the PROMETHEE multicriteria decision method

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Abstract. This article explores the use of multicriteria decision methods (MCDMs) to identify the optimum treatment for removing micropollutants from wastewater. With the increasing complexity of industrial and urban wastewater, which contains a wide range of micropollutants, it is becoming crucial to develop effective and sustainable treatment strategies. MCDMs provide a framework for evaluating a variety of treatments, considering several criteria, such as efficiency, cost, energy consumption, environmental impact and technical feasibility. This article examines different processing technologies and compares those using MCDM methods such as the preference ranking organization method for enrichment evaluation (PROMETHEE). Using this approach, this study proposes a systematic and objective method for identifying the most appropriate treatment options, facilitating more efficient wastewater management and protection of the aquatic environment.

1 Introduction

The progress of synthetic chemistry in the 20th century has allowed the development and production of many organic and inorganic molecules of interest [1, 2]. These molecules have various applications and are used in medicine, agriculture, chemistry or formulation [3, 4]. Some of these molecules are called micropollutants (MPs) because they present proven or suspected harmful effects even at low concentrations (from ng/L to µg/L) [5, 6]. As a result of human activities, these molecules can be found in wastewater [7, 8]. The three main types of sources are domestic, artisanal, industrial activities and road traffic: urban surfaces through rainwater runoff and pavement cleaning: and urban space maintenance practices and illicit acts [3, 9-12].The presence of micropollutants in the environment, particularly in water bodies, poses significant risks to ecosystems and human health. Aquatic organisms are particularly vulnerable to the effects of micropollutants. Even at low concentrations, these substances can disrupt the endocrine systems of fish and other wildlife, leading to reproductive and developmental issues, behavior changes, and even mortality. The bioaccumulation of these pollutants up the food chain further magnifies their impact, affecting not only aquatic life but also the animals and humans that depend on these water bodies for sustenance. This disruption of aquatic ecosystems can lead to reduced biodiversity and the impairment of the ecological balance and functions of water bodies [4, 10, 13-19]. The potential impact of micropollutants on human health is a growing concern. Through the consumption of contaminated water and food, humans are exposed to a cocktail of these substances, which could lead to long-term health effects. The trace levels of pharmaceuticals and endocrine-disrupting chemicals found in drinking water, for instance, are suspected to contribute to a range of health issues, including hormonal imbalances, reduced fertility, and an increased risk of certain cancers. Despite the low concentrations, the chronic exposure and mixture of various micropollutants raise questions about their synergistic effects and the true extent of their impact on human health [20-27]. The sources and impacts of micropollutants highlight the complexity of managing these pollutants in the environment. Effective strategies require a comprehensive approach that addresses the variety of sources and pathways through which these pollutants enter the environment, as well as the development of advanced treatment technologies to remove them from wastewater and drinking water. Additionally, public awareness and regulatory measures play crucial roles in reducing the release of these substances and mitigating their impacts on ecosystems and human health [2, 28-32].

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Wastewater treatment plants (WWTPs), which are designed to remove suspended solids, organic carbon, organic and ammonia nitrogen, and phosphorus, can remove some biodegradable MPs [11,12,33-37]. In contrast, hydrophilic MPs are little affected by conventional physical-chemical or biological treatments [38-42]. Among these MPs are many pharmaceutical residues and heavy metals that can reach receiving aquatic environments and have a negative impact on the environment [2,5,43,44]. Faced with these limitations of conventional systems, several solutions are being considered to eliminate these MPs before they reach the natural environment: reduction at the source, optimization of existing wastewater treatment systems and use of advanced treatments [45]. These techniques are less costly and environmentally friendly and have low energy consumption. Therefore, the question is how to choose the most efficient advanced treatment technique for the removal of these compounds from wastewater.

To do this, the solution adopted here consists of applying the multicriteria decision method (MCDM) in order to rank, from the best to the worst, the chosen hypotheses. As part of operational research, this method has been perfected by creating mathematical tools to facilitate the task of decision-makers [46]. The results of this analysis aim to discriminate the behaviour of the hypotheses considered and thus to judge their relative performance as a complement to a technical-economic analysis [45]. The different areas in which of MCDM is applied include including materials, energy, production, risk management, the environment, IT, and tourism [47-52]. The percentages of applications and the domains are presented in Figure 1.

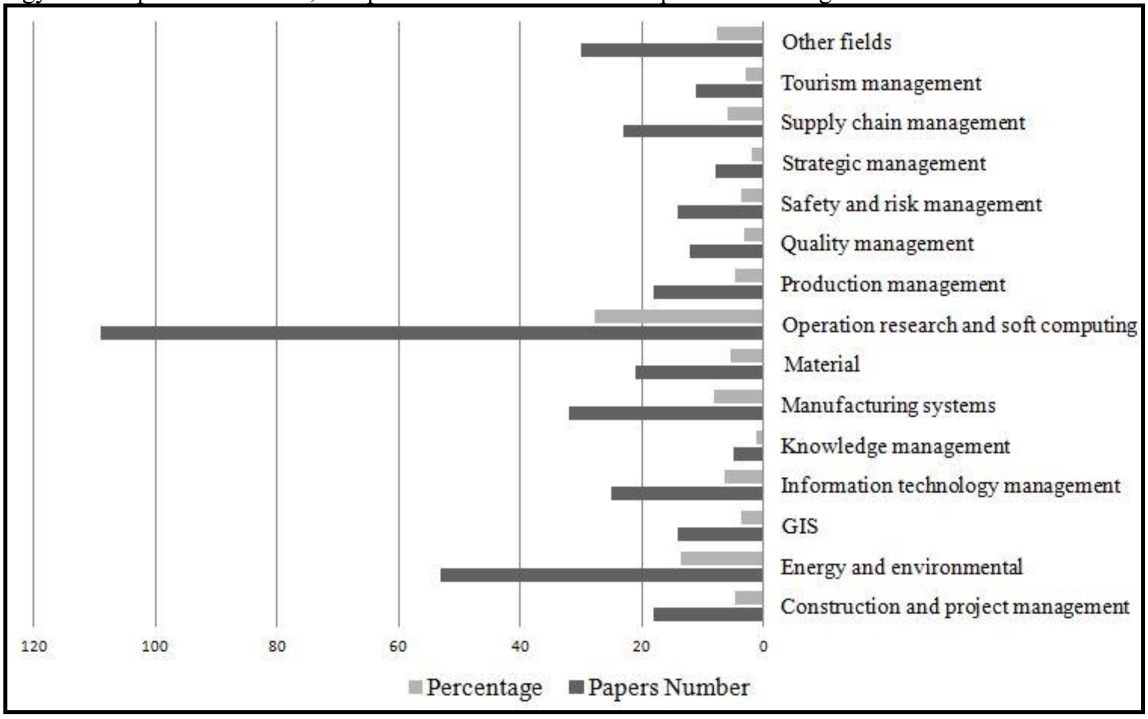

Fig. 1. Studies regarding MCDM and application areas.

The environment and energy domain had a share of 13.49%. This domain contains several specific subdomains in which they applied MCDM.

Among these subdomains are energy resources [53], risk sustainability [54], energy policies [55], transport sustainability [56], environmental management [57], renewable energy [58], and environmental quality [59].

Only 4% focused on the wastewater treatment subfield.

PROMETHEE is proposed in this study because it is considered one of the most important multicriteria decision-making techniques for analysing and selecting the most appropriate advanced technology for the removal of micropollutants from wastewater according to the considered criteria.

2 Literature Review

The presence of micropollutants in wastewater represents a major environmental and health challenge. These substances, often present in low concentrations, can nevertheless have harmful effects on the environment and human health. They are characterized by great diversity, including both organic and inorganic compounds. Pharmaceuticals and personal care products (PPCPs) include a wide variety of substances such as drugs (antibiotics, analgesics, and hormones), cosmetics and hygiene products. Their presence in wastewater is mainly due to human excretion after consumption of medicines, inappropriate discharge of unused medicines, and washing of cosmetics and hygiene products applied to the skin. These compounds can persist in the environment, posing risks to aquatic fauna and human health.

Pesticides and herbicides are widely used in agriculture and domestic gardening to control undesirable plant and animal pests. Their infiltration into surface and groundwater can occur through agricultural and urban runoff. These substances are of particular concern because of their bioaccumulation potential and toxicity to nontarget organisms.

This category comprises a wide range of substances, including volatile organic compounds (VOCs), phthalates, polychlorinated biphenyls (PCBs) and flame retardants. These chemicals originate from various industrial processes, consumer products and industrial waste. Their release into the environment can occur through direct industrial discharges into wastewater, as well as through the degradation of products containing these substances. Their persistence and toxicity pose significant risks to aquatic ecosystems and public health. The micropollutants in wastewater come from a multitude of sources, including domestic, agricultural and industrial activities. The diversity of these substances and their potentially harmful effects underscore the importance of developing effective treatment methods to eliminate them. The remainder of this study will focus on the evaluation of different treatment technologies using multicriteria decision methods to identify the optimum options for the elimination of these micropollutants. The management of micropollutants in wastewater represents a major challenge for current treatment technologies. While traditional wastewater treatment methods are effective at removing conventional organic and inorganic contaminants, the removal of micropollutants requires more advanced approaches. These technologies aim to reduce the concentration of these harmful substances to levels that minimize their environmental and health impacts. Table 1 provides an overview of the wastewater treatment methods currently used to eliminate micropollutants.

Table 1. Emergent wastewater treatment techniques.

Technology	Advantages	Disadvantages
Advanced Oxidation Processes (AOPs)	- Highly effective at breaking down complex pollutants. - Can treat a wide range of contaminants	- High operational costs - Potential for toxic by-product formation
Membrane Filtration	- Efficient removal of various micropollutants. - Chemical-free process	- Susceptible to fouling. - High energy and maintenance costs
Activated Carbon Adsorption	- High efficiency for certain pollutants. - Simple operation	- Need for regular carbon replacement. - Variable effectiveness across pollutant types
Biofiltration	- Utilizes natural processes. - Low operational costs	- Relatively slower process. - Performance affected by environmental conditions
Nanotechnology	- High efficiency even at low concentrations. - Specificity to pollutants	- Potential environmental and health risks of nanomaterials. - High costs
Ion Exchange	- Effective for targeted pollutants, especially metals. - Quick process	- Limited application range. - Need for resin regeneration
Photocatalysis	- Can degrade a wide range of pollutants. - Uses light energy, potentially renewable	- Requires specific catalysts, often expensive. - Efficiency depends on light availability
Electrocoagulation	- Effective for particulate and some dissolved pollutants. - Minimal chemical use	- Electrode replacement costs. - Generation of sludge requiring disposal
Ultraviolet (UV) Radiation	- Effective for disinfection and degradation of some chemicals. - No chemical additives needed	- Limited to pollutants sensitive to UV. - High energy consumption
Ozonation	- Strong oxidizing ability. - Effective for a variety of organic pollutants	- Ozone generation is energy-intensive. - Can produce harmful by-products in certain conditions

3 Methodology

3.1 PROMETHEE presentation

PROMETHEE, which stands for Preference Ranking Organization Method for Enrichment Evaluations, is a multicriteria decision support approach designed to handle situations where several criteria need to be considered simultaneously to evaluate a set of alternatives. Developed in the 1980s by Brans and Vincke, this method enables decision-makers to rank or select options by integrating their own preferences [60].

The process begins by clearly defining the evaluation criteria, which can vary from qualitative to quantitative. Once the criteria have been established, each alternative is evaluated according to these criteria, enabling comparison matrices to be constructed. The special feature of PROMETHEE lies in its use of preference functions to transform differences between alternative evaluations into degrees of preference, reflecting the way in which a decision maker values differences between options according to different criteria.

The method is divided into two main versions: PROMETHEE I for a partial ranking and PROMETHEE II for a complete ranking of alternatives [61]. This segmentation offers the flexibility to adapt the analysis to the nature of the decision to be made. The approach is also distinguished by its incorporation of a visual tool, GAIA (Geometrical Analysis for Interactive Aid), which helps to visualize the trade-offs between criteria and to understand the impact of these on the final decision [62]. In summary, PROMETHEE provides a rigorous methodological structure for dealing with the complexity inherent in multicriteria decision-making, facilitating the identification of a preferred solution or ranking of alternatives based on the decision-maker's specific preferences [63].

3.2 Study Design: Conceptual framework for comparing treatment methods.

In this research, PROMETHEE multicriteria decision-making (MCDM) techniques were utilized to evaluate and rank various options. The same options and criteria were considered when employing each method to address the proposed problem. Identifying a decision-maker is critical within the context of MCDM studies. A decision maker could be either an individual or a collective of experts (for instance, a board or committee) responsible for making the ultimate selection among the options. This study's assessments were conducted by three distinct decision-makers: the municipality, the wastewater treatment plant manager, and the local community.

3.3 Definition and weighting of criteria

The PROMETHEE method adopted similar criteria, albeit divided differently into clusters: "environmental, economic and technical". The percentile weights for each criterion were defined by expert opinions from the municipality (Municip), operators of the wastewater treatment plant (WWTP) and the local community (Local C). In the PROMETHEE approach, the criteria were redistributed between different clusters, with 25% attributed to disposal efficiency, 20% attributed to operational cost, 15% attributed to environmental impact, and 10% attributed to ease of implementation, 15% attributed to energy consumption and 15% attributed to sustainability. After collecting the necessary parameters for evaluating the wastewater treatment technologies, the Gaussian preference function was employed for every criterion, as detailed in Table 2. Subsequently, Visual PROMETHEE Decision Lab software was used to carry out the analysis.

4 Description of alternatives

The following section summarizes current treatment technologies for removing micropollutants from wastewater collected from recent studies.

Table 2. Visual PROMETHEE to identify the optimal WWT technology for the removal of micropollutants.

Criteria	**Removal efficiency**	**Operating cost**	**Environmental impact**	**Ease of implementation**	**Energy consumption**	**Sustainability**
Cluster	Environmental	Economic	Environmental	Technical	Economic	Economic
Weight (%)	25	20	15	10	15	15
Activated Carbon	8	5	7	6	5	9
Advanced Oxidation	9	6	8	5	7	7
Membrane Filtration	7	4	9	7	3	8
Biochar Adsorption	6	7	10	8	9	10
Electrochemical	7	5	6	4	6	6

4.1 Activated carbon adsorption

Activated carbon adsorption (A1) is a widely used treatment technique for the purification and depollution of water and air [28, 64, 65]. This method relies on the use of activated carbon, a form of carbon treated to create a large porous surface capable of capturing contaminants. The principle of adsorption is based on activated carbon's ability to attract and retain pollutant molecules on its surface, enabling them to be separated from the medium in which they are found.

The manufacture of activated carbon generally involves the carbonization of carbon-rich materials, such as wood, coconut shells or agricultural residues, followed by activation [33, 66-78]. Activation can be achieved by high-temperature heat treatment in the presence of oxidizing agents, which increases the porosity of the material and thus increases its specific surface area. This high specific surface area makes activated carbon extremely effective at adsorbing a wide range of substances, including organic compounds, certain heavy metals and chlorine residues.

In water treatment applications, activated carbon is used to eliminate unpleasant tastes and odours, volatile organic compounds (VOCs), pesticides and pharmaceuticals, thereby improving drinking water quality [79-81]. For air treatment, activated carbon effectively captures gaseous pollutants, organic vapours and odours, helping to clean indoor air and control industrial emissions. The choice of activated carbon and the design of the adsorption system depend on many factors, including the nature and concentration of the pollutants to be eliminated, and the volume of fluid to be treated. The regeneration of activated carbon, which enables it to be reused, is also an important aspect of its industrial and environmental application, offering a solution that is both effective and sustainable for the treatment of polluted water and air.

4.2 Advanced oxidation processes

Advanced oxidation processes (A2) (AOP) represent a set of chemical treatment techniques used for water and air pollution control, and are characterized by the use of powerful oxidizing reagents to degrade organic and inorganic pollutants to less harmful or harmless compounds. These techniques take advantage of chemical reactions involving free radicals, particularly the hydroxyl radical (-OH), which is known for its high reactivity and ability to oxidize a wide range of contaminants [82, 83].

The principle of AOPs is based on the in situ generation of hydroxyl radicals from various combinations of oxidants and energy. Commonly used methods include ozonation, UV photolysis, hydrogen peroxide (H_2O_2), and combined systems such as ozone/UV, H_2O_2/UV, and the Fenton process (H2O2/iron). These systems can effectively breakdown substances that are difficult to treat by traditional biological or physicochemical methods, such as persistent organic compounds, dyes, pesticides and endocrine disruptors.

The application of AOPs in water treatment aims to improve drinking water quality, treat industrial and municipal wastewater, and restore contaminated groundwater. The effectiveness of these methods depends on a number of factors, including the type and concentration of pollutants, the composition of the water matrix, and the operating conditions of the process.

4.3 Membrane filtration

Membrane filtration (A3) is a separation technology that uses semipermeable barriers to remove or concentrate particles and dissolved substances from liquids [84, 85]. This method relies on the size of the membrane pores, which allow the passage of certain components while retaining others, depending on their size, charge or chemical affinity. Membrane filtration is widely used in water and wastewater treatment, drinking water production, and the food, pharmaceutical and biotechnology industries for applications such as desalination, purification, product concentration and contaminant removal. There are different types of membrane filtration methods classified according to pore size: reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). Each of these technologies has its own specific application, depending on separation needs. Reverse osmosis, with its finer pores, is used to remove ions and small molecules, while microfiltration, with its larger pores, is suitable for separating larger particles, such as bacteria and sediments. The advantages of membrane filtration include high separation efficiency, relatively low energy consumption compared with thermal separation methods, and the ability to operate at ambient temperature, which is particularly important for the treatment of heat-sensitive substances. However, the challenges associated with this technology include membrane clogging, which can reduce efficiency and increase operating costs, and the need for periodic membrane cleaning and replacement. Research continues to develop more clogging resistant and durable membranes to make this technology even more efficient and economical.

4.4 Biochar Adsorption

Biochar adsorption (A4) is an emerging water and air treatment technique that uses biochar as an adsorbent material to remove pollutants. Biochar is a carbon-rich char produced by the pyrolysis of plant biomass, such as agricultural residues, forestry waste or organic waste, in a low-oxygen environment. This treatment method takes advantage of biochar's porous structure and high specific surface area, which enable it to capture a variety of contaminants, including heavy metals, volatile organic compounds and pesticides [86, 87].

The biochar adsorption process is considered ecologically sustainable and economically viable because as it valorizes biomass waste and can be implemented with low environmental impact. In addition to its effectiveness in purifying water and air, biochar also contributes to carbon sequestration, thereby reducing greenhouse gas emissions. Current research focuses on optimizing the adsorbent properties of biochar, such as its porosity, specific surface area and surface functionalities, to improve its effectiveness in removing specific pollutants. The adaptation of biochar for targeted applications, its regeneration and recycling after saturation and the assessment of its overall environmental impact are important aspects currently being studied to maximize the benefits of this promising technology.

4.5 Electrochemical oxidation

Electrochemical oxidation (A5) is an advanced wastewater treatment technique that uses redox reactions occurring at the surface of electrodes to degrade organic and inorganic pollutants. This method relies on the application of an electric current between electrodes immersed in the wastewater, generating powerful oxidizing species such as hydroxyl radicals, chlorine or ozone directly in the medium to be treated. These reactive species are capable of breaking the chemical bonds of pollutants, leading to their mineralization or transformation into less harmful compounds [88,89].

One of the main advantages of electrochemical oxidation is its ability to treat water containing recalcitrant or toxic pollutants, which are difficult to remove by conventional biological or physicochemical methods. In addition, this technique offers the advantages of easy integration into existing treatment processes, does not require the addition of external chemical reagents, and can be modulated according to the pollutant load and volume to be treated.

However, the success and efficiency of electrochemical oxidation are highly dependent on the type of electrode used, operating conditions such as the applied current and pH, and the specific nature of the pollutants present in the water. Ongoing research in this field is aimed at developing more efficient and durable electrode materials, optimizing treatment parameters and assessing the environmental and economic impact of this technology for wider and more effective application in wastewater treatment.

4.6 Sustainability and ecosystem impacts

The sustainability and ecological impact of water treatment technologies are critical considerations in their long-term application and environmental integration. These considerations span the entire lifecycle of the technology, from material sourcing and energy consumption to waste generation and disposal.

Activated carbon adsorption is a widely employed method for removing various contaminants from water, offering high efficiency and broad applicability. Its sustainability is primarily challenged by the carbon's lifecycle, from production to disposal. The production of activated carbon, often from non-renewable sources like coal, can be energy-intensive and contribute to greenhouse gas emissions. Additionally, the disposal of spent activated carbon, which may be laden with hazardous contaminants, poses significant environmental risks if not properly managed. Innovations in activated carbon regeneration and the exploration of more sustainable raw material sources, like agricultural by-products, are vital for improving its long-term sustainability and reducing its ecosystem impacts [13].

Advanced oxidation processes (AOPs), involving the generation of highly reactive species capable of degrading persistent pollutants, are notable for their effectiveness against a wide range of contaminants. However, the energy intensity of these processes, especially those requiring UV light or ozone generation, raises concerns about their long-term sustainability. Moreover, the potential formation of toxic by-products from the incomplete degradation of pollutants necessitates careful consideration of downstream impacts on aquatic ecosystems. Efforts to enhance the energy efficiency of AOPs and to develop more effective post-treatment strategies are essential for mitigating these impacts [82, 83].

Membrane filtration technologies, such as reverse osmosis, ultrafiltration, and nanofiltration, are at the forefront of removing various pollutants due to their high efficiency and selectivity. The sustainability of membrane technologies is primarily affected by the energy required for operation and the lifespan of the membranes themselves. Membrane fouling, a common issue, exacerbates energy consumption and necessitates frequent membrane replacement, contributing to waste. Moreover, the disposal of concentrate waste streams poses additional environmental hazards. Advancements in membrane materials to reduce fouling and energy consumption, alongside effective waste management strategies, are critical for enhancing the sustainability of these technologies [85].

Biochar adsorption presents a promising, more sustainable alternative for water treatment, leveraging the adsorptive properties of biochar derived from biomass. The use of waste biomass as a feedstock and the potential for biochar to be regenerated or repurposed as a soil amendment after its adsorptive life highlight its sustainability benefits. However, the ecological impacts of biochar depend on its source and production process, which must be managed to avoid negative outcomes such as deforestation or the misallocation of agricultural resources. Research into the long-term effects of biochar on soil health and carbon sequestration is vital for fully realizing its environmental benefits [90].

Electrochemical oxidation offers a chemical-free approach to degrading pollutants through the application of electric currents, marking it as an innovative method with potentially lower direct environmental impacts. The method's sustainability largely hinges on the energy source used and the efficiency of the electrochemical process. The use of renewable energy can significantly enhance its sustainability profile. Furthermore, the technology's reliance on electrode materials, which may involve rare or toxic metals, poses sustainability and disposal challenges. Developing more sustainable electrode materials and recycling strategies is crucial for minimizing these impacts [91].

In summary, the sustainability and ecological impacts of water treatment technologies are multifaceted, encompassing energy use, material sourcing, and waste generation and management. Enhancing the long-term sustainability and reducing the ecological footprint of these technologies require ongoing innovation in material science, process engineering, and energy management. Through concerted efforts in these areas, the water treatment industry can move toward more sustainable and ecologically harmonious practices.

5 Results and discussion

Table 3 and Fig. 2 present a multicriteria decision analysis ranking different wastewater treatment methods using Visual PROMETHEE. Biochar adsorption stands out at the top of the list, demonstrating a superior net flux and a strong preference for positive outflow, indicating that it is largely favoured over other methods while rarely being outperformed, as evidenced by its low negative outflow. Advanced oxidation ranks second, showing a decent balance of being preferred over other methods while facing some competition. Activated carbon is in the middle of the ranking, with a slightly negative net flux, suggesting a balance between its advantages and disadvantages. Membrane filtration is below the midpoint, less frequently favoured in comparisons and more commonly outperformed by alternatives. Electrochemical treatment is ranked lowest, with the highest negative outflow, indicating that it is most often outperformed by other methods in terms of efficiency. This analysis suggested that biochar adsorption is the leading option for micropollutant removal according to the criteria evaluated.

As shown in Fig. 2, biochar adsorption and advanced oxidation had predominantly positive values, indicating that they are generally preferred across the evaluated criteria, such as removal efficiency, ease of implementation, sustainability, and environmental impact. Biochar adsorption shows a notably high preference for sustainability, suggesting that it scores exceptionally well in that criterion. Advanced oxidation exhibited a strong positive effect on removal efficiency, indicating its effectiveness in eliminating micropollutants.

Activated carbon shows a balance with some criteria falling into the positive and others are falling into the negative. This might imply that while it performs well in some areas (such as environmental impact), it may not be as effective or preferred for other criteria (such as removal efficiency). Membrane filtration and electrochemical oxidation have criteria that mostly fall below the neutral line, indicating less preference for these methods compared to others. In particular, electrochemical oxidation has a significant negative effect on removal efficiency, suggesting that it is the least effective method for removing pollutants removal among those analysed.

The overlapping labels in the graph may indicate that the criteria share similar weights or scores for the treatment methods or that there could be a visual overlap due to the design of the graph. Overall, the graph suggests that biochar adsorption is the most preferred method according to the criteria assessed, followed by Advanced Oxidation, while Electrochemical Oxidation is the least preferred method.

Table 3. Ranking of the best treatments for removing micropollutants.

Ranking	Methods	Net flow	Positive outflow ranking	Negative outflow Ranking
1	**Biochar Adsorption**	0.6667	0.8333	0.1667
2	**Advanced Oxidation**	0.1667	0.5833	0.4167
3	**Activated Carbon**	-0.0417	0.4583	0.5
4	**Membrane Filtration**	-0.2083	0.375	0.5833
5	**Electrochemical**	-0.5833	0.1667	0.75

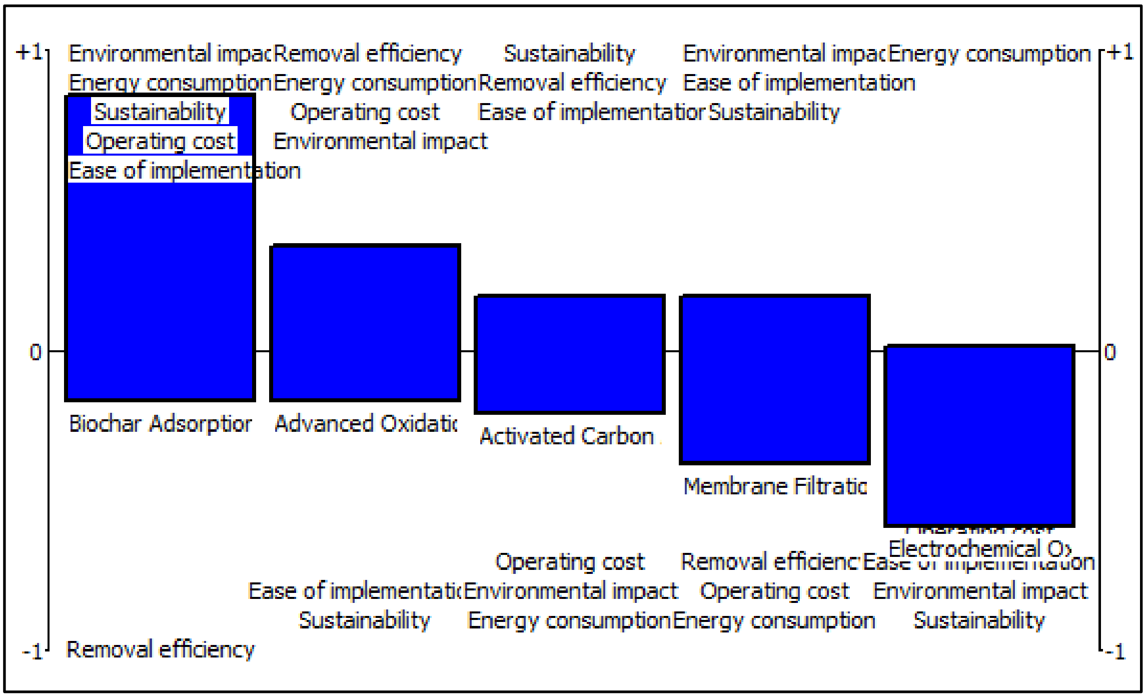

Fig. 2. Evaluation of treatment techniques

Conclusion

In conclusion, the application of the fuzzy PROMETHEE decision-making tool has demonstrated its utility as an effective means for selecting the most preferred method among various wastewater treatment technologies based on our analysis. The findings indicate that biochar adsorption has emerged as the leading method, with advanced oxidation processes being the second most favoured option for wastewater treatment. These results may vary depending on the context, such as in developing regions where a consistent power supply is a concern, which could affect the feasibility of certain technologies. A deeper exploration of the PROMETHEE methodology and its comparison with other decision-making approaches would be advantageous, for assisting decision-makers and organizations—both governmental and nongovernmental—in making informed choices, not only in engineering but also across diverse fields of study. For future research, incorporating additional criteria is suggested, as the more extensive the criteria considered, the more robust the reliability of the outcomes, and conversely, the fewer the criteria, the less reliable the outcomes may be.

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