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A Multi-Criteria Decision-Making Approach to Evaluate Different UVC/H_2O_2 Systems in Wastewater Treatment

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Abstract: High azoxystrobin (AZO), difenoconazole (DFZ), and imidacloprid (IMD) pesticide removal rates in sixteen bench-scale experiments concerning tomato washing water treatment were obtained through a UVC/H_2O_2 advanced oxidative process. Experimental conditions ($[H_2O_2]_0$) and irradiance (E_{UVC}) were optimized for higher degradation rates (pseudo-first-order reaction). To consider both economic aspects and environmental impacts when defining the treatment technology, as well as technological requirements, this study applied a multi-criteria decision-making method (MCDM) to assess and differentiate similar UVC/H_2O_2 process configurations. This allowed for the identification of the cheapest experimental arrangement with the lowest associated environmental impacts, coupled to the highest degradation rate (k_{IMD}). After consulting experts to determine the importance of the applied criteria and measuring alternative performances, experiment E7 ($[H_2O_2]_0$ = 43.5 mg L^{-1}; E_{UVC} = 15.0 W m^{-2}; k_{IMD} = 0.236 s^{-1}) was determined as meeting the three criteria in a balanced manner. Although E7′s technological performance regarding degradation rate did not achieve the best individual result, it presented the lowest impacts and costs among the analyzed series, although alternatives are sensitive to decision-maker priorities. This study considered different factors of a process displaying potential industrial applications still in the design stage to achieve a more efficient and balanced solution.

Keywords: UVC/H_2O_2; pesticides; wastewater treatment; multi-criteria decision making; life cycle assessment

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1. Introduction

Brazil is currently one of the largest agricultural producers worldwide and, since 2008, the main pesticide consumer on a global scale [1,2]. A total of 620,000 tons of active ingredients (AIs) were consumed, and 321 new products were registered in this class during the 2019–2020 biennium alone. Based on this performance, experts and sector observers forecast a significant increase in pesticide contributions in the country's trade balance for the next decades [3,4]. Due to advances in analytical technologies, pesticides, along with pharmaceuticals, personal care products and steroid hormones, whose effects concerning environment disposal are not yet understood, are regarded as compounds of emerging concern, displaying the potential to cause harmful effects on living organisms and ecosystems, even if released in low concentrations [5].

Effluents from the tomato washing process constitute a significant threat to humans, and the environment exposure route to these compounds, alongside extensive pesticide use in agriculture, soil transport, and sprinkler equipment washing, constitutes a prominent factor in water body contamination. Prior to fruit processing to generate consumer goods and their derivatives, tomatoes are unloaded on conveyor belts and water is used for transport and surface washing. At this stage, pesticide residues not absorbed by these fruits before harvesting may be transferred to the aqueous phase [6,7]. As conventional effluent treatment processes (i.e., coagulation, filtration, sedimentation) do not completely remove these compounds, due to their high chemical stability and low biodegradability [5,8,9], Advanced Oxidation Processes (AOPs) constitute an efficient alternative for the treatment of these contaminants. The UVC/H_2O_2 technology is noteworthy in this context, reducing the hazards of contaminated effluents to limits capable of preserving the integrity of receiving bodies, and even enabling water reuse in agroindustry operations.

In general terms, the UVC/H_2O_2 process consists in generating hydroxyl radicals (HO•) by breaking the O—O bond of hydrogen peroxide molecules (H_2O_2) through ultraviolet (UVC) radiation [10]. The UVC/H_2O_2 process distinguishes itself from other AOP modalities due to its potential for microorganism inactivation, thanks to the use of UVC radiation, easy storage, and handling, given the high solubility of hydrogen peroxide and implantation and operation simplicity, on account of the high organic pollutant degradation capacity by direct photolysis or due to the action of hydroxyl radicals [10,11].

UVC/H_2O_2 application in the treatment of effluents containing pesticides has been extensively explored in the literature [12–17]. Concerning tomato rinse water disinfection, this process has been reported as achieving high removal rates of the contaminants azoxystrobin (AZO), difenoconazole (DFZ) and imidacloprid (IMD) [18], which are constituents of several commercial products applied in Brazilian crops for pest control [3]. However, studies on the use of UVC/H_2O_2 as a treatment alternative concentrate efforts on the investigation of technological aspects, such as its compound degradation ability and the influence of the aqueous matrix and operational parameters on process performance. On the other hand, for a treatment logic to be adequate for a modern design and management conducts, it must also achieve good results for other factors, such as economic performance and environmental impacts [19,20]. A consistent way of meeting this last requirement is through the application of the Life Cycle Assessment (LCA), a technique capable of quantifying adverse environment and human effects from resource extraction to final deposition processes [21].

The LCA has been successfully applied in assessments seeking to identify AOP-associated impacts or aiming to compare the environmental performance of this class of treatment technologies on different operation scales [22–29], always following ISO 14040 and 14044 standards [21,30]. These include some assessments concerning arrangements created for the decontamination of effluents containing pesticides [31,32]. Studies describing the use of LCA in verifying the environmental performance of the UV/H_2O_2 process in any type of situation are still, however, lacking. Furthermore, although some recent reports are available, scientific records concerning actions that examine the economic aspects of AOP technologies are also scarce [33–35]. In general, these diagnoses are concerned with quantifying fixed and variable costs or assessing the economic viability of different AOP arrangements in large-scale enterprises.

In addition to an attractive academic challenge, the consideration of further elements of the technical performance of a treatment that aims to reduce pesticide release into the environment is a mandatory conduct to support decision-making processes involving the management of this technology. This is because the use of multiple criteria can alter the optimal conditions of the arrangement if these are defined by only observing technological-operational perspectives. In this regard, the Multi-Criteria Decision-Making (MCDM) technique is an approach recommended for situations of this kind, as it indicates the most adequate path among a set of alternatives based on criteria considered important for a specific type of analysis with both precision and scientific support [36]. Furthermore, the MCDM's ability to simultaneously deal with qualitative and quantitative data, including expert opinions, makes it a commonly applied technique by decision-makers [37], including in situations involving the choice of adequate wastewater treatment methods [38–47]. However, although these studies also focus on technology comparisons, their developments associated to AOP are rare [48,49].

The Simple Multi-Attribute Rating Technique, (SMART), proposed by Edwards in 1971 [50], is noteworthy among the MCDM methods due to its simplicity, requiring only simple answers from the decision-maker based on their preferences, analyzing results in an uncomplicated way, and the high efficiency rate of its diagnoses. Even though SMART cannot fully capture the divergent opinions of various decision-makers, in most situations, due to their rationality and opportunistic behavior when faced with a decision, it has been proven robust and safe for many applications, while also offering a better understanding and analysis of a specific problem [51].

Considering these characteristics and particularities, this study applied the SMART, as an MCDM method, to evaluate different system UVC/H_2O_2 configurations applied to the treatment of tomato rinse water, to identify the best results in terms of technological, environmental, and economic factors (criteria). Technological performance tests (decision-making process alternatives) were carried out in a bench-scale facility using a synthetic effluent prepared with typical AZO, DFZ and IMD concentrations and the factors were evaluated by experts.

The innovative character of this study manifests itself in the use of a scientific decision-making approach to develop a more efficient and balanced treatment process with potential industrial applications, simultaneously considering technological, environmental, and economic perspectives. Moreover, this experience also seeks to encourage the consideration of different analysis dimensions not only in already installed processes, but also during the design and project phases of new initiatives.

2. Materials and Methods

This study was guided by the conceptual framework that defines the SMART method, which comprises the following activities: (i) problem description and alternative and criteria definition; (ii) establishment of measurement methods; (iii) determination of the degrees of importance (weight) of the selected criteria; (iv) provisional decision; and (v) a sensitivity analysis [51]. Each of these procedures will be detailed below based on the conduct, actions, and assumptions within the scope of this initiative.

2.1. Problem Description and Alternative and Criteria Definition

The project from which this research originates from investigated the influence of initial H_2O_2 concentrations ($[H_2O_2]_0$) (x_1) and irradiance (x_2) on the performance of the UVC/H_2O_2 system in the treatment of tomato rinse water contaminated by the three active ingredients AZO, DFZ and IMD. To this end, a solution was prepared with nominal concentrations of 3.0, 2.0 and 3.0 mg L^{-1} of AZO, DFZ and IMD, respectively, and sixteen laboratory experiments were carried out in a benchtop photochemical reactor, differing only in terms of system configurations [18]. These characteristics were established through the application of a sequential Doehlert design [52], a resource often applied in experimental designs. Table 1 describes the values of (x_1) and (x_2) for each experiment. Such conditions remained unchanged during the development of this research.

In general terms, a Shimadzu ultra-fast liquid chromatograph (UFLC, LC 20AD) was used to monitor the decay of the concentration of active ingredients during the tests. The equipment disposes of a UV/VIS detector (SPD 20A) and a C18 column (250 × 4.60 mm, 5-µm particle size). A 1.0 mL min^{-1} mobile phase of Milli-Q® water (A) and acetonitrile (B) was used, and elution occurred in gradient mode: 50% B (0–3 min); increase to 80% B (3–12 min); 80% B (12–14 min); decrease from 80 to 50% B (14–18 min). The oven temperature was maintained at 40 °C, and the injection volume was 100 µL. The analysis determined AZO and DFZ pesticides at 254 nm and IMD at 270 nm. Furthermore, according to the methodology provided by [53], calibration curves were constructed and both the limit of detection (LOD, mg L^{-1}) and limit of quantification (LOQ, mg L^{-1}) were calculated for each pesticide: LOD_{AZO} = 0.166, LOQ_{AZO} = 0.331; LOD_{DFZ} = 0.199, LOQ_{DFZ} = 0.397; and LOD_{IMD} = 0.128, LOQ_{IMD} = 0.255.

Table 1. Experimental UVC/H_2O_2 assay conditions following the Doehlert design for two variables and pseudo-first-order specific degradation rates for each investigated pesticide.

Run	(x_1) $[H_2O_2]_0$ (mg L^{-1})	(x_2) Irradiance (E_{UVC}) (W m^{-2}) [(1)]	k_{AZO} (s^{-1})	k_{DFZ} (s^{-1})	k_{IMD} (s^{-1})
E1 [(2)]	62.2	21.8	1.648	0.520	0.397
E2 [(2)]	62.2	21.8	1.599	0.513	0.412
E3 [(2)]	62.2	21.8	1.659	0.549	0.423
E4	99.5	21.8	1.940	0.617	0.412
E5	80.9	28.6	1.764	0.725	0.548
E6	24.9	21.8	0.898	0.360	0.441
E7	43.5	15.0	0.857	0.352	0.236
E8	80.9	15.0	0.974	0.507	0.277
E9	43.5	28.6	1.608	0.515	0.435
E10	118	28.6	1.806	0.726	0.562
E11	118	15.0	1.010	0.530	0.287
E12	137	21.8	2.998	0.671	0.465
E13	37.3	21.8	0.888	0.425	0.409
E14	31.1	28.6	0.970	0.572	0.312
E15	12.4	21.8	0.679	0.331	0.280
E16	18.9	15.0	0.475	0.226	0.182
E17	31.1	15.0	0.535	0.244	0.194
E18	18.7	28.6	0.770	0.297	0.369

(1) Irradiances E_{UVC} = 15.0, 21.8 and 28.6 W/m^2 correspond to 2, 3 and 4 lamps, respectively. (2) For subsequent analyses, experiments E1, E2 and E3 are treated as E1-2-3, and the mean value will be applied. Source: Adapted from [18].

All experimental conditions defined from the Doehlert design resulted in the removal of the investigated compounds below detection limits after a continuous irradiation period of 15 min. Degradation rates were noted as sensitive to initial hydrogen peroxide concentrations and the number of lamps used in each arrangement based on the pseudo-first-order reaction rate values (k_{AZO}, k_{DFZ} and k_{IMD}), which were estimated from the results of each experiment (Table 1), and the relationship of these indicators with the corresponding amounts of (x_1) and (x_2). A statistical analysis allowed for the development of response surface models for k_{AZO}, k_{DFZ} and k_{IMD}, and indicated the optimal experimental conditions in terms of initial H_2O_2 concentrations and irradiance for the highest pseudo-first-order degradation rate, resulting in an adequate and robust technological performance concerning pollutant removal.

Following the completion of this stage, the analysis continued to determine the environmental impacts and costs associated with each arrangement operation. For a better understanding of the problem, economic performance was described based on the '*Costs*' criteria and subdivided into '*Reagent costs*' and '*Energy costs*'. The '*Degradation Rate*' was chosen to specify the technological dimension, while the impacts caused by the arrangements in the form of '*Primary Energy Demand*' and '*Global Warming Potential*' portrayed the environmental dimension.

After establishing the indicators for all dimensions, the test performances were compared and ranked. The evaluation of these alternatives was carried out using the V.I.S.A.®—v 8 software [54], which is designed to support studies conducted applying the MCDM technique. Due to its versatility, the V.I.S.A.® provides the means for the user to organize and synthesize information in a simple way, while also enabling the exploration of change implications in decision-making values and/or priorities [54].

2.2. *Performance Measurement of Alternatives*

2.2.1. Technological Performance

In terms of technological performance, k_{imd} values were always lower than k_{azo} and k_{dfz} (Table 1), thus configuring the most delicate and demanding situation in terms of decontamination. IMD removal required high amounts of material and energy inputs, being, therefore, also responsible for the highest costs and environmental impacts. Because of this, k_{imd} values were chosen as criteria for performance characterization regarding the experiments in this dimension.

Because of the small magnitude of the constants, centesimal-based relative scale was applied to classify the results. From this, a 'zero' score was assigned to the lowest value of the entire series (e16: k_{imd} = 0.182 s^{-1}), and a '100' score to the highest congener (e10: k_{imd} = 0.562 s^{-1}). In a context in which the technological behavior of the system is described by pollutant degradation rates, this indicator directly influences the global performance of the investigated alternatives.

2.2.2. Economic Performance

Reagent Costs corresponded to the expenses concerning preparation of the H_2O_2 solutions used in the tests, therefore varying according to this input's concentrations. Energy Costs were estimated from the total electricity consumption by the equipment comprising the process scheme. Even though electrical consumptions due to stirring and temperature control are common, this parameter fluctuates between different scenarios, according to the number of UVC lamps used in each situation. A unit cost of USD 0.15/kWh was applied to the utility, which corresponds to the annual average 2019 value for the city of São Paulo under regular consumption conditions, that is, outside peak tariff periods. If represented by costs, the economic dimension will exert an inverse influence on the overall performance of the options evaluated during decision processes.

2.2.3. Environmental Performance

The environmental impacts associated with the experiments were estimated by applying the LCA technique in the attributional modality and employing the 'cradle-to-gate' application scope. Following the methodological guidelines provided in the ISO 14044 standard [30], the UVC/H_2O_2 technology was evaluated in its variations, for a Reference Flow (RF) comprising '*remove AZO, DFZ and IMD contaminations present in 150 mL of tomato rinse water below detection limits*'. This approach is common in such circumstances, given that LCA studies with similar characteristics have been conducted with the expectation of providing support for managerial decision-making processes and have been successful in their purposes. In this context, developments in the fields of the selection of productive arrangements for biofuel and derivative syntheses are highlighted [55,56], as well as closing water circuit [57–59], cattle raising [60], domestic solid waste management [61] and energy planning.

Primary data described the consumptions and emissions directly associated with the application of the UVC/H_2O_2 process for each variation. The life cycles for utilities (i.e., energy generation, transport and tap water treatment), obtaining inputs ($H_2O_{2(sol\cdot)}$, synthesized by autooxidation from the balance established between anthraquinol and anthraquinone in the presence of oxygen and hydrogen), and system element manufacturing (lamps, electrical components, and accessories) were modelled from secondary data. The Brazilian electricity grid was specified by parameters obtained from the National Energy Balance (BEN) 2021 [62], while lamp manufacturing and H_2O_2 solution preparation were detailed based on the datasets that make up the Ecoinvent® database [63]. In these cases, however, some adaptations concerning electrical and thermal energy sources, water treatment, and, when necessary, input, and intermediary transport were applied, so the inventories could portray the conditions under which these elements are produced in Brazil. Multifunctionality situations were not identified throughout the life cycles of the evaluated systems.

The impacts in the form of Primary Energy Demand (PED) were dimensioned by the Cumulative Energy Demand (CED)—v 1.11 method, which quantifies the energy resource depletion from renewable sources (biomass: RB; water: RW; and solar, wind and geothermal: RSWG), and non-renewable fossil: NRF, biomass: NRB; and nuclear: NRN) [64]. Global Warming Potential (GWP) estimates were carried out by applying the IPCC 2013 GWP 100a—v1.03 method [65]. The quantification of these performance indicators took place using the SimaPro®—v 9.1 software, which is regularly employed in environmental diagnoses formulations of a systemic nature.

2.3. Determining the Level of Importance (Weight) of the Selected Criteria

To determine the level of importance (or weight) of the investigated criteria in the decision-making process, a survey was carried out with experts working in different areas. The graduation profile defined for these participants included Engineers, with an emphasis on the Chemical and Environmental modalities, as well as bachelor's in Chemistry and Business Administration. Figure 1 describes the respondent profiles in terms of academic background. Working fields with the highest frequency rates for this professional universe included teaching and research activities related to environmental matters and liquid effluent treatment and management. Finally, it should be noted that the average practice period by the consulted specialists was 7.4 years.

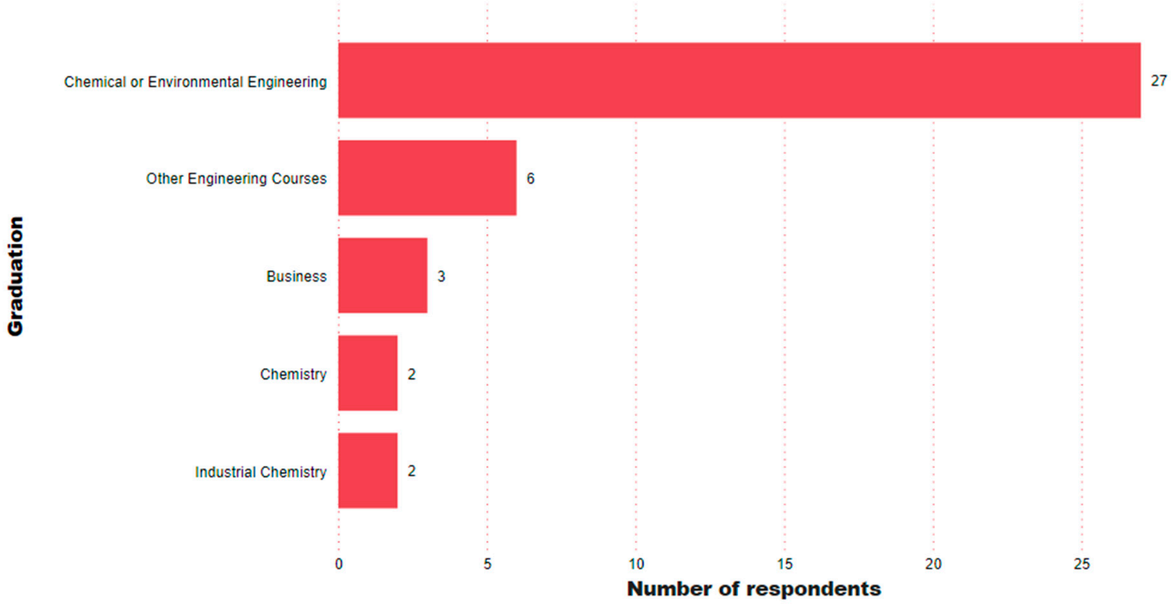


Figure 1. Interviewee graduation profiles.

Figure 2 displays the value tree constructed from the defined criteria and subcriteria, and their attributed weights by the experts alongside their cumulative results. Value trees provide better decision-making problem visualization and understanding.

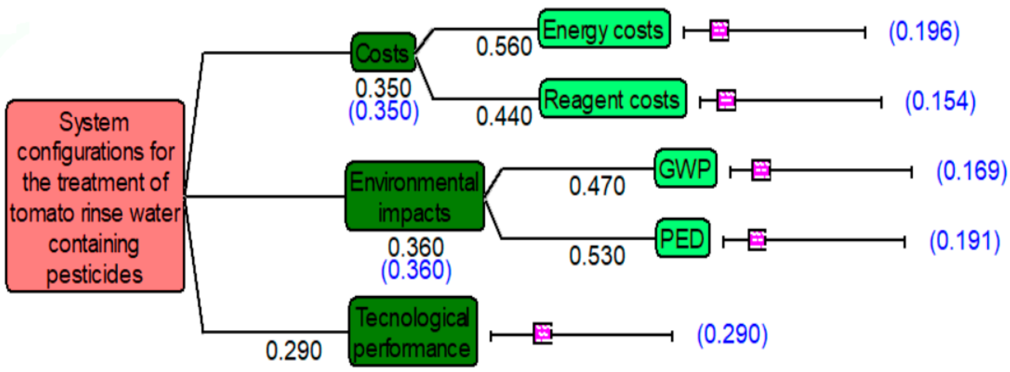


Figure 2. Value tree for evaluating the employed UVC/H_2O_2 process system configurations. In black: weights assigned to the evaluated criteria and sub-criteria; in blue: cumulative weights.

The survey gathered a total of forty specialists. Guided by a questionnaire, respondents were encouraged to assign grades to the investigated criteria (Technological, Economic and Environmental) and sub-criteria (Economic: Reagent Costs and Energy Costs; and Environmental: Primary Energy Demand and Global Warming Potential) analyzed by a search. To do so, each participant used a scale ranging from 'zero' (least important) to 'ten' (highest importance). In addition, the sum of the portions assigned to each criterion and pair of subcriteria should totalize 'ten' points.

After completing the grading step, the results were normalized to an arbitrary scale of limits between 0 (least preferable) and 100 (most preferable). The average mode and median of the sample were then determined for these conditions. The parameter analysis revealed a convergence of values, suggesting that the average could be adopted for weight distribution. Furthermore, it is interesting to note that the largest and most representative portion of respondents (~68%) comprised Chemical and Environmental Engineers. According to [66], when a predominance of individuals with the same level of expertise or information access is noted in a group of participants, it is possible to expect high response correlations. In these cases, the average value becomes the best representation of interviewee judgement.

3. Results and Discussion

3.1. Economic Performance Profile of Different UVC/H_2O_2 System Configurations

Table 2 describes the results of the Reagent and Energy Costs associated with each investigated alternative and the criteria and sub-criteria valuation concerning the experimental configurations for the UVC/H_2O_2 system. The arrangement composition has a significant impact on Reagent Costs. This finding is supported by the fact that the difference between minimum and maximum estimated values for this parameter varies by over 12-fold. Therefore, as they consume a greater mass of H_2O_2, experiments E10, E11 and E12 presented the highest Reagent Costs of the entire series. On the other hand, the lowest expenditures were observed in tests E15, E16 and E17, which fulfill the same function with lower oxidant concentrations.

Table 2. Criteria and subcriteria valuation for the investigated UVC/H_2O_2 system configurations.

Run	Costs		Technological Performance	Environmental Impacts	
	Reagents (USD/RF)	Energy (USD/RF)	k_{IMD} (s^{-1})	PED (MJ/RF)	GWP (g $CO_{2\ eq}$/RF)
E1-2-3	0.00011	0.0449	0.411	2.03	51.8
E4	0.00018	0.0449	0.412	2.03	51.8
E5	0.00015	0.0452	0.548	2.04	52.1
E6	0.00005	0.0449	0.441	2.03	51.8
E7	0.00008	0.0446	0.236	2.01	51.3
E8	0.00015	0.0446	0.277	2.01	51.3
E9	0.00008	0.0452	0.435	2.04	52.1
E10	0.00022	0.0452	0.562	2.04	52.1
E11	0.00022	0.0446	0.287	2.01	51.3
E12	0.00025	0.0449	0.465	2.03	51.8
E13	0.00007	0.0449	0.409	2.03	51.8
E14	0.00006	0.0452	0.312	2.04	52.1
E15	0.00002	0.0449	0.280	2.03	51.8
E16	0.00003	0.0446	0.182	2.01	51.3
E17	0.00006	0.0446	0.194	2.01	51.3
E18	0.00003	0.0452	0.369	2.04	52.1
Value scale	0.00002–0.00025	0.0446–0.0452	0.182–0.562	2.01–2.04	51.3–52.1
Preference	Lower value	Lower value	Highest value	Lower value	Lower value

A linear value curve was constructed for each criterion, attributing 0 (zero) and 100 (one hundred), respectively, to the worst and best performance of each analyzed series. Therefore, each value in Table 2 is now described by a relative index on the same scale. For example, the cost of reagent E15 (0.00002 USD/RF) constitutes the lowest value in the series that describes this economic dimension component. Due to this characteristic, it describes the best of the costs in question, thus receiving an index of 100 on the relative scale. Following the same approach, the cost of reagent E12 (0.00025 USD/RF) was assigned an index of 0, as it represents the highest (or worst) of the values in the same set. Note that the value curves created for the cost and environmental impact subcriteria are inversely proportional to the value scale (preference). Finally, preferential independence among criteria was checked.

Energy Costs are directly related to the volume (150 mL) of effluent from tomato washing treated by different UVC/H_2O_2 system configurations. These values exhibited much more discrete variations (~1.34%) between the minimum and maximum measurement range limits than Reagent Costs, as the energy demands of the evaluated arrangements are restricted to the electrical consumption required for UVC irradiation.

3.2. Influence of System Configurations on Environmental Impacts

Table 2 also presents the environmental performance results described in the form of Primary Energy Demand (PED) and Global Warming Potential (GWP) generated during the experiments to remove AZO, DFZ and IMD present in 150 mL of tomato rinse water. As was noted for Energy Costs, PED and GWP values were decisively influenced by the electricity consumption of each arrangement and, for this reason, also presented practically invariable profiles.

Hydropower plants accounted for 65% of the total energy generation in Brazil in 2019. This was followed by contributions from thermoelectric plants operating with natural gas, hard coal, oil and derivatives and biomass (23%), wind farms (8.6%), nuclear power plants (2.5%), and photovoltaic complexes (~1.0%) [62]. This composition allows us to explain the higher impacts (38% or 771 kJ/RF) in the form of Renewable Water in the accumulated PED results of all tests. The combustion of biomass derived from sugarcane bagasse in thermoelectric plants that present combined cycle technology adds another 28% of contributions in the form of Renewable Biomass to the Primary Energy Demand of UVC/H_2O_2 systems, due to the Gross Calorific Value intrinsic to this fuel (4.95 MJ/kg sugarcane) [55].

Finally, contributions from Non-Renewable Fossils (NRF) burning with high High Heat Values (HHV) are also relatively high (24%). This is the case of natural gas, whose average HHV value (38.3 MJ/m^3) makes this a source of 53% of the added NRF impacts, hard coal (HHV = 19.1 MJ/kg) with a 26% contribution to the PED subcategory, and oil and derivatives (HHV = 45.8 MJ/kg), which participate with another 21% of the adverse Non-Renewable Fossils effects.

Given its prevalence in the environmental performance of the UVC/H_2O_2 system, electricity consumption was also the main cause (82%) of GWP impacts. In this case, however, thermoelectric sources concentrated the highest contribution rate for the category, of 29.1 g $CO_{2\,eq}$/RF. The results derive from the combustion of natural gas in conventional plants (33%), which operate under combined cycle (12%), hard coal (41%), oil derivatives (14%), and even biomass (~1.0%) sources. In addition, hydropower plants contribute another 13.3 g $CO_{2\,eq}$/RF.

Fossil CO_2 is noteworthy among the GWP impact precursors, as it is emitted at a rate of 33.9 g/RF due to fossil fuel burning (natural gas, hard coal, and oil derivatives). This is followed by CO_2 losses due to land transformation actions (8.27 g/RF) motivated by the advance of sugarcane cultivation over areas that previously hosted other crops or cattle raising practices. CH_4 emissions, in fossil form (43.4 mg/RF) due to incomplete natural gas combustion in thermoelectric power plants, and biogenic form (290 mg/RF), due to the non-oxidation of carbon present in the biomass during cultivation area cleaning and in the formation of hydroelectric lakes, also play an important role in the composition of global GWP impacts.

Finally, N_2O losses to air that also contribute to GWP occur due to (i) combustion processes that use atmospheric air as oxidant and (ii) biomass burning. In the latter case, nitrogen is associated to the fuel structure due to fertilization by N-fertilizers, in particular, urea. As observed for costs, the environmental impact results vary inversely with the performance of alternatives in decision-making processes.

3.3. MCDM in Evaluating the UVC/H_2O_2 System Configurations

3.3.1. Ranking of the Alternatives

Figure 3 displays the alternative ranking obtained herein following the additive model, which involves the sum of weighted values for each criterion.

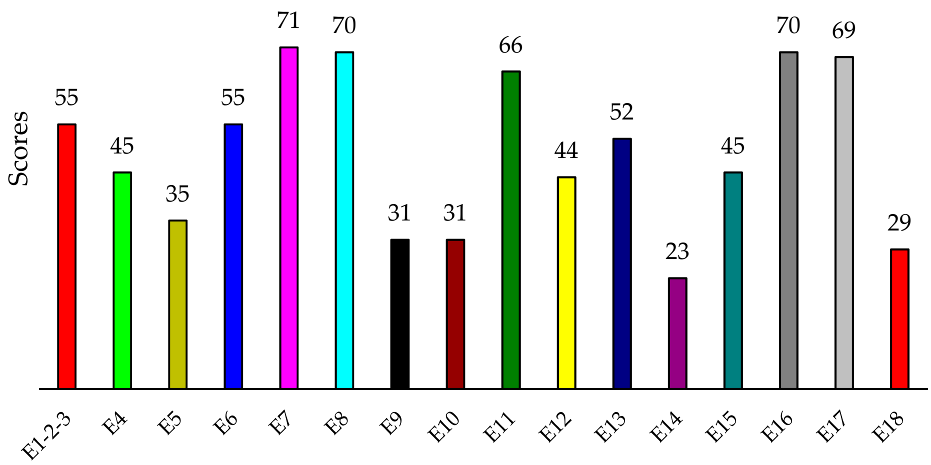


Figure 3. Ranking of the alternatives.

The recommended alternative regarding performance was Experiment E7, whose final performance reached a total of 71.0 points. This test comprises a process configuration of two lamps (E_{UVC} = 15.0 W/m^2) and $[H_2O_2]_0$ = 43.5 mg L^{-1}. From a technological perspective, its k_{IMD} value was not the highest (0.236 s^{-1}) among the alternatives. However, as the number of lamps exerts a significant influence on costs and on the environmental impacts associated with the arrangements, this experimental configuration is the most advantageous concerning these aspects. In other words, a slow process and with a smaller number of lamps met the three criteria considered by the analysis in a balanced manner. E7 was followed by E8 and E16, at 70 points each, as well as E17 (69 points) and E11 (66 points). Despite the same number of lamps for these experiments, the addition of oxidizing species at higher concentrations increased Reagent Costs for E8 and E11, a preponderant factor for the choice of the experiment, even though the technological performance of these arrangements surpassed the first place (k_{IMD} = 0.277 s^{-1}). On the other hand, in the specific cases of E16 and E17, even though the Reagents Costs are lower than in E7, these alternatives achieve a worse technological performance than E7.

The worst option comprised E14 (23.0 points), which despite a higher k_{IMD} value (0.312 s^{-1}) compared to E7, displays a combination of the most unfavorable costs and environmental impacts, associated to the highest number of lamps (E_{UVC} = 28.6 W/m^2) among all options. As the global results were very close, a comparison between the applied criteria and the sensitivity analysis are interesting options to differentiate the performance of the alternatives, exhibiting variations concerning systems configuration.

3.3.2. Comparison between the Applied Criteria Regarding Decision Making and Sensitivity Analysis

A criteria comparison was performed to determine their influence on the decision (Figure 4a–c). The first set of Technological Performance versus Costs (Figure 4a) indicated that E5, E6, E10 and E16 are at the efficiency frontier. By valuing technological performance over costs, the chosen experiment would be E10. In contrast, the worst technological performance and lower cost would be E16, followed by E17.

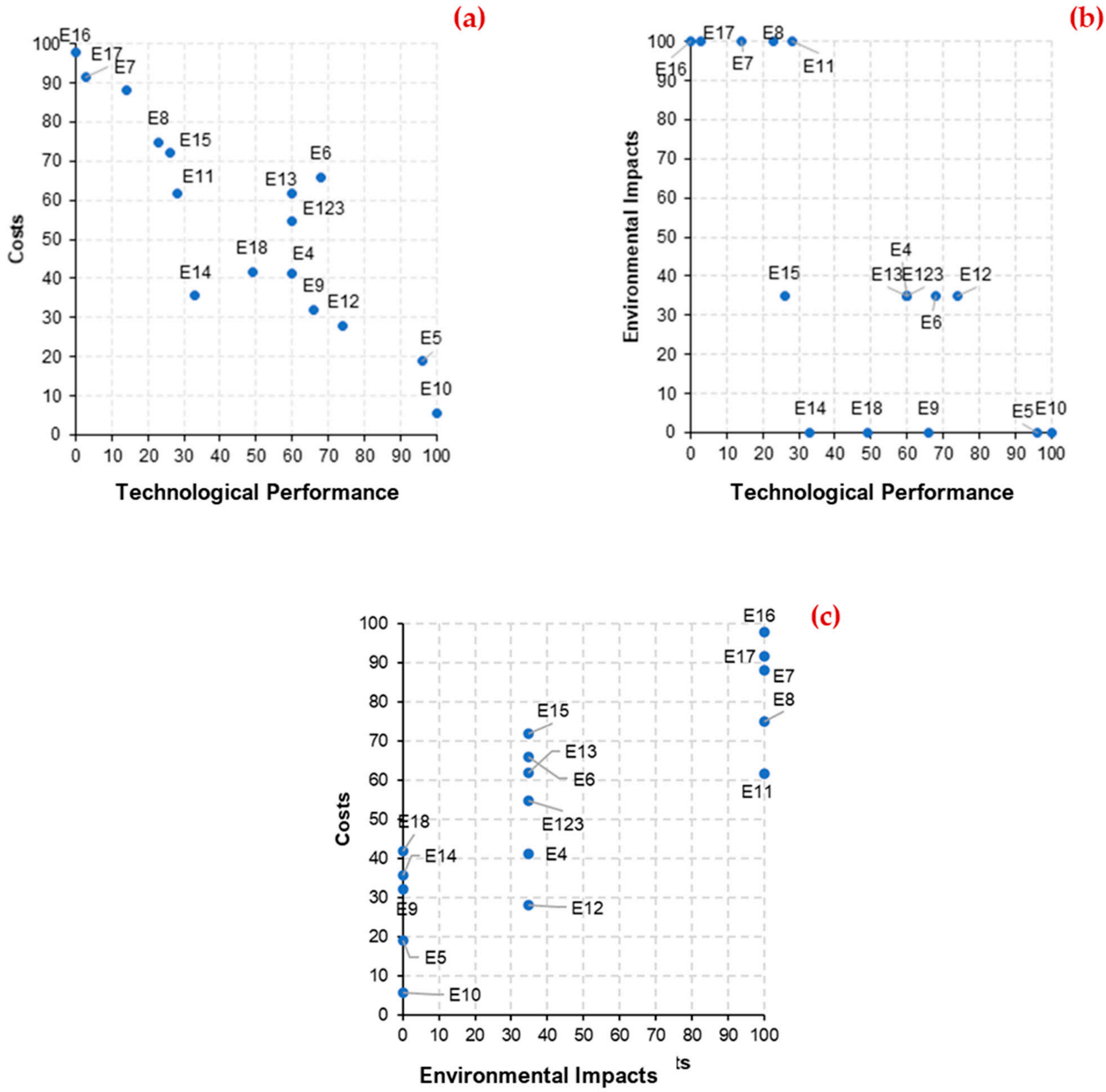
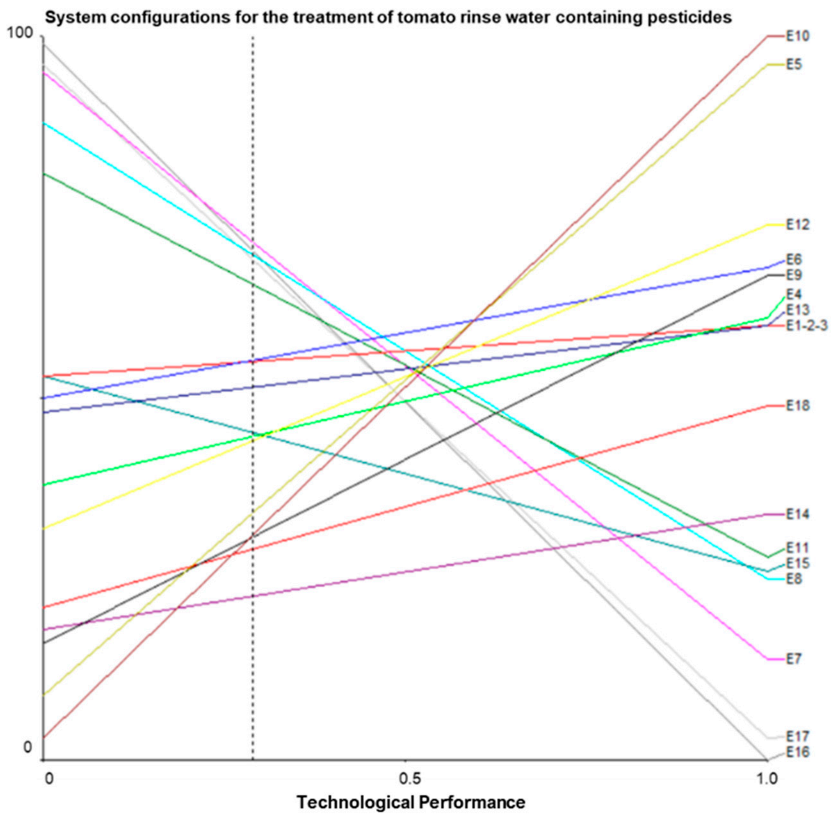
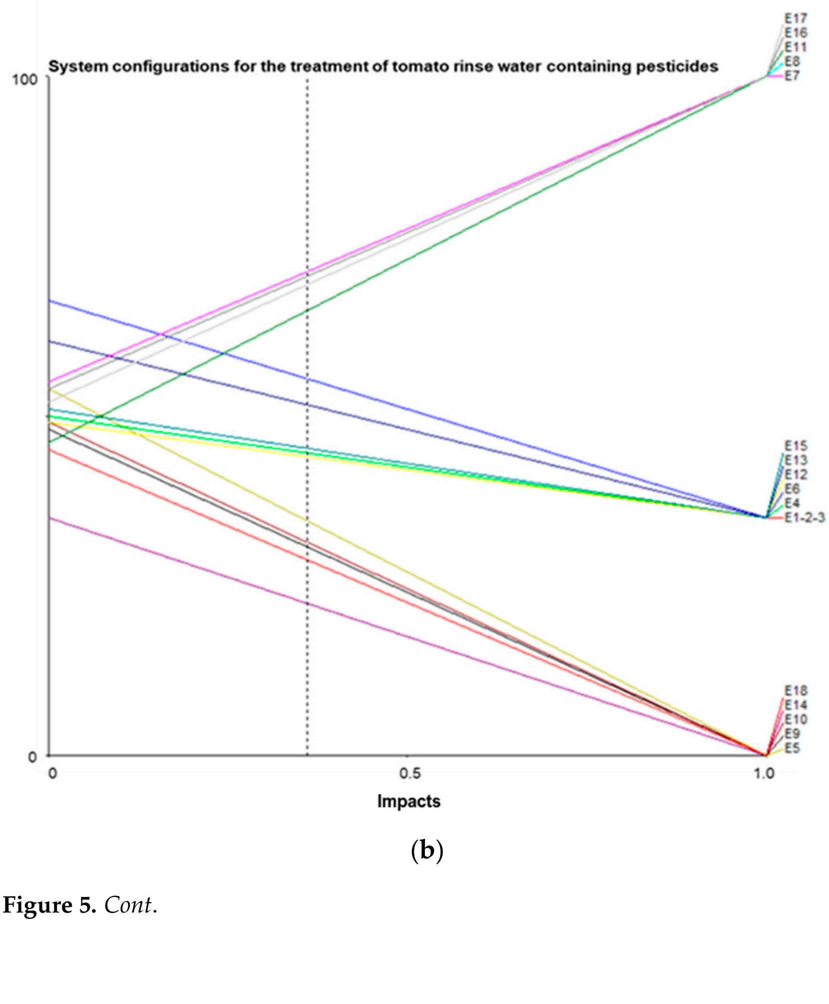


Figure 4. Comparison of the investigated criteria. (**a**) Technological Performance vs. Costs; (**b**) Technological Performance vs. Environmental Impacts; and (**c**) Environmental Impacts vs. Costs. Note: The values for the alternatives shown on the axes result from the value curves.

The same is noted for the relationship between Technological Performance and Environmental Impacts (Figure 4b). Finally, to coordinate the Environmental Impacts and Costs (Figure 4c), the alternatives exhibiting lower costs and environmental impacts (better performance) were E16, E17 and E7. Alternatives E8 and E11 display high impacts, but other alternatives exhibit higher costs. The Sensitivity Analysis (SA), described graphically in Figure 5a–c, indicates how robust the choice of alternatives to change is.

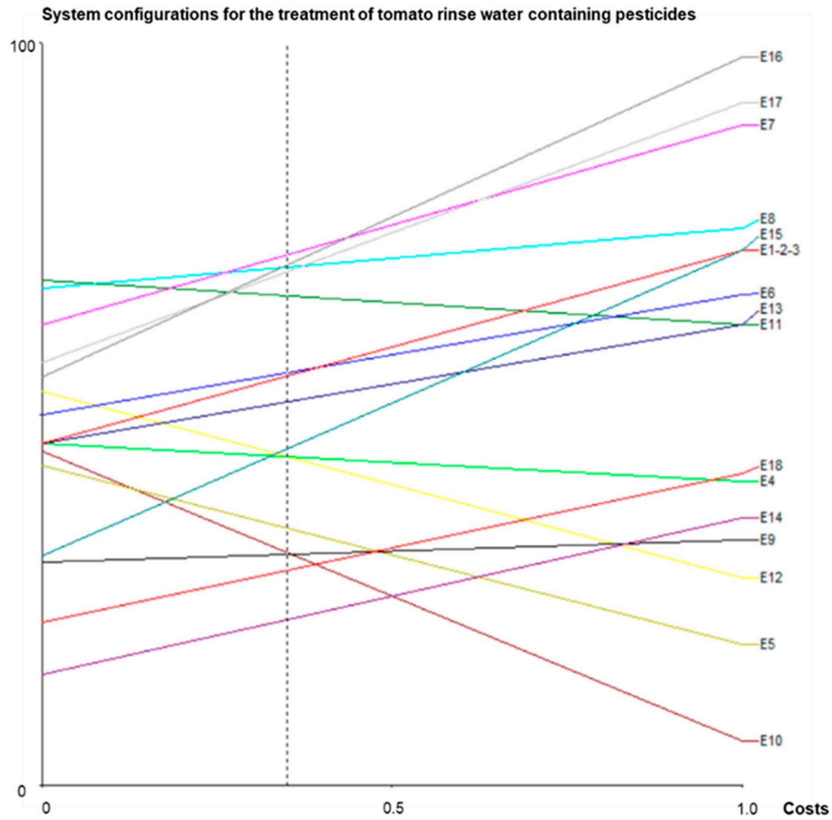


(**a**)



(**b**)

Figure 5. *Cont*.



(**c**)

Figure 5. Sensitivity analysis of alternative selections concerning the investigated criteria. (**a**) Technological Performance effects on the choice of alternatives; (**b**) Environmental Impact effects on the choice of alternatives; and (**c**) Cost effects on the choice of alternatives. Caption: The dashed line indicates the current weight of the evaluated criterion.

The SA results indicate that the choice of alternatives changes when varying criteria importance. When the method is applied to Technological Performance (Figure 5a), if the weight of this criterion is less than 0.50, the choice is between experiments E7 and E16. However, from that point onward (weight $\geq$ 0.50), E7 is no longer the most recommended choice. Furthermore, as the importance of Technological Performance approaches 1.0, the choice tends to E10. Such behavior was somewhat expected, given the similarity between the experiment impacts and costs, and the fact that E10 has the highest k_{IMD} value. In this context, priority is given to the speed of reaction, depreciating the costs and environmental impacts generated during the process to achieve active ingredient decontamination in tomato rinse water.

Concerning the analysis involving Environmental Impacts (Figure 5b), increased weight makes the choice of alternatives converge to the set formed by E7, E8, E11, E16 and E17, which presented corresponding PED and GWP impact values, accounting for the number of lamps in their structures. Finally, by valuing lower costs (Figure 5c), the choice tends towards E16, whose combination of reagent costs and energy is the lowest possible. In addition, some alternatives are not susceptible to weight variation, such as E13, as low reagent costs are offset by intermediate energy costs and low PED, by mean GWP values, aside from a slightly above average k_{IMD}. The SA allows the decision-maker to obtain further knowledge on the problem, potentially leading to criteria reconsideration during the establishment of the applied technology and the choice of another system configuration.

4. Conclusions

The sixteen experiments evaluated concerning the UVC/H_2O_2 process were shown to cause environmental impacts of a similar order of magnitude regarding Potential Energy Demand and Global Warming Potential, with very similar Reagents and Energy Costs. The observed variations are mainly due to the number of lamps used in the experimental setup and the oxidant concentrations, increasing costs and impacts.

Regarding the technological performance criterion, the k_{IMD} values were chosen to verify the best experiment in a worst-case scenario, since the values for the pseudo-first-order reaction rate for this AI were generally lower than those obtained for k_{AZO} and k_{DFZ}. Even though the Doehlert planning analysis indicated an optimal experimental value, aiming only at greater degradation speeds, when considering the associated environmental impacts and the process costs, Experiment E7, whose k_{IMD} value was not the highest (0.236 s^{-1}), was considered as presenting the best performance in meeting the three criteria.

The sensitivity analysis demonstrated that the increasing importance of technological performance leads to a change in choice towards the alternative with higher k_{IMD} (0.562 s^{-1}). On the other hand, if the environmental impact criterion were to be considered the most important, the choice would be between experiments E7, E8, E11, E16 and E17, which present the lowest associated impacts. Finally, the choice tends towards experiment E16 when the smallest cost combination is considered. Considering the low magnitude of the values and the small difference between the global performance of the investigated alternatives, the combination of the three criteria does, in fact, influence their performance. In the case of technology establishment, altering decision-maker priority can also alter he system configuration choice.

In addition to equating tomato washing effluent treatment alternatives in technical, economic, and environmental terms, the main contribution of this study lies in the simultaneous consideration of criteria that describe different dimensions and perspectives, which present different forms of measurement, and weights, which describe their degrees of importance, in the opinion of specialists, even during the design phase of the treatment arrangement. The SMART method application enabled the differentiation of very similar alternatives, and the choice of the most recommended experimental configuration. This method is robust and allows for the evaluation of a set of criteria (with different measurements and weights), and scaling results (alternatives). New alternatives can be added for model evaluation, i.e., the model can be replicated to other processes and configurations.

This study's limitations comprise the following: (i) the scale of the investigated process, which makes it impossible to further analyze associated costs and (ii) the choice of weights made after consulting the group of experts. Even though the consulted technicians display both knowledge and experience in the area, assessments by a more extensive and differentiated group could provide new information and insights regarding the chosen experimental configuration. However, and on the other hand, method robustness was confirmed by requiring a large weight variation, so changes in the choices of alternatives could be postulated. Moreover, although SMART was applied to choose operational alternatives herein, described by the sixteen laboratory tests, the evaluation criteria, using MCDC, provided a significant result variation, indicating important changes in the configuration process, which would be difficult to analyze without applying such an approach.

As almost natural consequences of this investigation, we suggest the expansion and reproduction of the effluent treatment process from tomato washing be carried out on other scales and considering other criteria (and therefore measurement methods), the respective non-linear value curves (representing values aligned with the decision-maker's preference), new weights (and weighing methods, such as wing weights cases [51], and Rank Order Centroids [67]), and a set of alternatives to be evaluated by the decision-making model.

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