Selection of Iron-based Additives for Enhanced Anaerobic Digestion of Sludge using the Multicriteria Decision-Making Approach

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Abstract – Enhancement of anaerobic digestion is vital for substrate solubilization and increased biogas production at a reduced cost. The use of several iron-based additives has proven effective in improving overall bio-digester performance during anaerobic digestion sludge. This study evaluates different iron-based additives for the selection of the best additive from the alternatives using a multi-attribute decision making (MADM) approach. The weights of the attributes were computed with the entropy weight technique and the ranking of the alternatives were performed using order preference by similarity to ideal solution (TOPSIS) method. Five attributes and thirteen frequently used alternatives were selected for evaluation. The result showed that additive cost and dosages were assigned the highest weight of 62.37 % and 27.46 %, respectively. Based on the performance scores of 99.15 %, 20 mg/L of Fe3O4 nanoparticles (Fe3O4 NPs-20) ranked best (number 1) among considered alternatives for enhancement of anaerobic digestion of sludge. The outcome of this evaluation agrees with previous experimental results and suggests that the choice of an effective iron-based additive should be based on its biogas enhancement potential and cost-effectiveness (low dosage requirement and low price).

Keywords – Additives; entropy method; iron-based; MADM; TOPSIS

1. INTRODUCTION

The unsustainable and environmentally menacing impacts of fossil energy sources have necessitated the global quest for renewable energy options. Biogas production via anaerobic
digestion technology is one of the many renewable alternatives with the dual role of waste management (treatment and reduction) and energy generation. Anaerobic digestion, which is a four-stage biochemical process involves the degradation of polymeric organic matter to monomers and simple molecules but is largely hampered by the nature of substrates, presence of inhibitor, nutrient deficiency, etc. [1]. The stage most affected is the hydrolysis stage, which is often referred to as the rate-limiting phase [2].

More so, due to the low substrate biodegradability occasioned by earlier mentioned challenges, various intensification strategies for improved biodegradability, reduced hydraulic retention time and increased biogas yield have been devised. These efforts include co-digestion, substrate pretreatment, additive/nutrient supplementation, etc. [1], [3]. Co-digestion of more than one substrate with complementary advantages aid maintenance of reaction pH, attainment of appropriate carbon-to-nitrogen (C/N) ratio and other nutrient range, reduction of possible toxicity and increase in organic loading rate of the bioreactor [4], [5]. Similarly, many substrate pretreatment types have been studied and reported to have enhanced substrate solubilization and hydrolysis rate via the alteration of intercellular structures of organic matter, disruption of sludge flocs, polyvalent ions, the cell wall of organisms and extracellular polymeric substances (EPS) [6]. Different pretreatment options, which are largely selected based on their cost-effectiveness and have been used for anaerobic digestion enhancement are categorized as physical (mechanical, hydrothermal, irradiation, etc.), chemical (dilute acid, alkaline, organosolv, oxidizing agents, etc.), biological and enzymatic (bacterial and fungal) and combined (thermochemical, physicochemical, etc.) [1], [7].

Although these enhancement options could improve substrate solubilization and increase biogas production, Zhao et al. [8] reported that the increase in biogas produced as a result of these pretreatment options may not compensate for the additional energy and chemical cost. Similarly, biological pretreatment type is time-consuming and extreme pH, salt formations and overall toxicity arising from the use of chemical pretreatment option tend to limit these options [9], [10].

Conversely, supplementation of the anaerobic digestion process with eco-friendly, cost-effective, and efficient additives as an enhancement option improves biogas quantity and quality [11], [12]. These additives aid the growth of anaerobes, enhance substrate solubilization and improve overall process biochemistry [13]. Some of these additives previously used for enhancement of anaerobic digestion are either as trace elements or nanoparticles of selenium (Se), cobalt (Co), iron (Fe), molybdenum (Mo), etc. [4], [14]. Due to some obvious advantages such as their low cost, ease of use and access and other biochemical benefits, iron-based additives have been mostly used for anaerobic digestion enhancement [15], [16].

Furthermore, previous studies have reported on the enhancement strides of iron-based additives. Zhang et al. [17] reported that the introduction of 100 mg/L of Fe3O4 nanoparticles, increased methane yield from anaerobic digestion of sludge by 58.7 %. Similarly, Casals et al. [15] reported the use of a novel, optimal and continued release of Fe3O4 NPs to the digester to achieve a 180 % rise in biogas yield. In the same vein, the addition of 15 mg/l Fe nanoparticle enhanced cattle manure by 38.2 % [18] It was also reported that the use of 100 mg/l trace iron aided the improvement of biogas recovery from food waste digestion [19]. There are varieties of iron-based additives that are being used for the enhancement of anaerobic digestion, but the selection of the appropriate iron-based additive could be a challenge due to the variation in properties and substrate types. This necessitates a systematic approach to selecting iron-based additives for the enhancement of anaerobic digestion.
The multiple attribute decision-making (MADM) approach, which is an aspect of the multicriteria decision-making (MCDM) system, is an established system for making the best decision from varying alternatives based on quantifiable and available attributes [1], [20]. Multiple attribute decision-making has been found useful in every sphere of science, engineering and technology and fast tracks and simplifies the task of selecting among alternatives [21]. Several multiple attribute decision-making methods can be stochastic, fuzzy, deterministic, or combined in nature, include priority, outranking, distance and mixed methods [1]. The established multiple attribute decision-making techniques among others are weight product method, weight sum method, analytical hierarchical process (AHP), compromise and goal programming, elimination and choice translation reality (ELECTRE), multiple attribute utility theory (MAUT), preference ranking organization method for enrichment evaluation (PROMETHEE) and technique for order preference by similarity to ideal solution (TOPSIS) [1], [7], [20], [22], [23]. It could be observed from previous studies that TOPSIS and AHP methods are the most used for decision making.

Previously, researchers have applied multiple attribute decision-making methods in selecting the best from alternatives especially in renewable energy studies [24]. Oluah et al. [23] used both TOPSIS and entropy method to select the best phase change material (PCM) for solar energy storage with the Trombe wall. They implemented the entropy method by assigning weights to phase change material identified properties and the PCM were ranked using TOPSIS by assigning performance scores within the interval of \( \{0,1\} \) for alternatives. For anaerobic digestion-related activities, Rao and Baral [20] used TOPSIS and a graphical method to rank feedstocks from available alternatives based on 30 predetermined attributes. On enhancement of anaerobic digestion, Ghandi et al. [25] reported the use of the Vise Kriterijumska Optimizacija I Kompromisno Resenje (VIKOR) technique to determine the best pretreatment on food waste for anaerobic digestion. It was observed that hotel food waste exposed to thermal pretreatment at 100 °C for 10 minutes ranked best with the VIKOR techniques and agrees with the experimental result too. Vannarath and Thalla [1] reported the evaluation and ranking of seven pretreatment methods with five attributes of lignocellulosic waste using TOPSIS and mixed technique of design of experiment and TOPSIS (DOE-TOPSIS). It was reported that the experimental and model results agreed with each other and showed the best pretreatment option for lignocellulosic waste for anaerobic digestion.

As shown above, studies on other forms of anaerobic digestion enhancements exist, but the absence of studies on iron-based additive selection techniques for enhancement of anaerobic digestion from available literature has necessitated this study. Selecting appropriate additive from alternatives for anaerobic digestion enhancement will improve digester performance, increase biogas yield, and reduce operational cost. Based on the available additives, six attributes vital to adjudicating the performance of biodigesters were considered in this study. This study also used entropy weight technique and TOPSIS methodology, which are novel to the selection/ranking of additive from alternatives to enhance biogas production.

2. **Methodology**

2.1. *Desirable Attributes of Anaerobic Digestion and Criteria for Additive Selection*

Suitable iron additives for the enhancement of anaerobic digestion processes must have some key features. The selected iron-additive should be of low capital and operational costs, apply to a wide range of substrates, and ultimately increase biogas yield and methane content [11]. These iron-based additives should be able to promote the growth of methanogen, facilitates direct interspecies electron transfer in syntrophic methane production, improve
Various desirable parameters/attributes on which anaerobic digestion performance is dependent include moisture content, volatile and total solids, temperature, odour, colour, volatile fatty acids (VFA), C/N ratio, alkalinity, pH, lignocellulosic content, biochemical oxygen demand (BOD), chemical oxygen demand (COD), heavy metals, ammonia, nature, cost, and availability of substrates, etc. [1], [20]. Similarly, the iron-additive enhanced anaerobic digestion process depends on the additive type, dosage, availability, type of substrate, cost of additives, etc. [26]. However, the selection of iron-based additive for enhanced biogas production is often based on its ability to enhance the removal of solids, increase methanogenic activities, improve system stability, increase VFA conversion and removal, increase organic loading rate, reduce hydraulic retention time, increase biogas yield, low dosage usage and low additive cost, etc. According to Cioabla et al. [27], the above-listed attributes are largely dependent on each other and variations in any affects the attribute, hence our multicriteria approach to selecting and ranking iron-based additives.

In this study, all the selected iron-additives were used for enhancement of anaerobic digestion of sludge, with attributes as categorized in Rao and Baral [20] such as physical attributes (Volatiles solids removed, %), chemical (COD removed, %, VFA removed, %) and others (biogas increase, %, additive cost and dosage).

2.2. TOPSIS Technique

This technique is a widely accepted numerical method of solving multiple attribute decision-making challenges, its conceptual framework developed by Hwang and Yoon [28]. It is based on the selection of the best alternative from one with the least Euclidean distance from the positive ideal solution and the farthest Euclidean distance from the negative ideal solution [1], [23]. In this work, the TOPSIS approach was deployed for ranking iron-based additives enhanced anaerobic digestion of sludges with process performance as the attributes of interest. These procedures were followed:

1. Vital attribute selection.
2. Entropy weight determination.
3. TOPSIS analysis and priority list selection.

The attributes and alternatives of choice are depicted in Fig. 1 with a decision matrix chart.

2.2.1. Vital Attribute Selection

Only application-specific and relevant attributes were chosen from all the attributes stated above for iron-based enhanced anaerobic digestion. These attributes include % volatile solids (VS) removed, % COD removed, % VFA reduced, % improvement in biogas yield, dosages, and additive cost. The additive costs were sourced in US dollars from Sigma-Aldrich and Indiamart, they were also calculated based on dosages of iron-based additives used by researchers cited in this work. Other less relevant attributes were not considered.
2.2.2. Weight Determination by Entropy Method

This important weight model uses the probabilistic approach to evaluate the uncertainty in information [23]. The entropy weight method has a highly objective result because its operation is largely devoid of human factor interference and dependent on the available data, hence, it better than other subjective models [29]. A decision matrix is used once there are m alternative and n attributes for the determination weights using the entropy method Eqs. (2)–(4).

The decision matrix contains the values of attributes arranged in a column and the matching of the alternatives arranged along the row to get a matrix as shown in Eq. (1).

\[
X = \begin{bmatrix}
X_{11} & X_{12} & \cdots & X_{1n} \\
X_{21} & X_{22} & \cdots & X_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
X_{m1} & X_{m2} & \cdots & X_{mn}
\end{bmatrix},
\]

where, alternatives \( i \) ranges from 1 to \( m \) (1, 2, 3, \ldots, \( m \)) and its corresponding attributes \( j \) ranges from 1 to \( n \) (1, 2, 3, \ldots, \( n \)). \( X_{ij} \), which is the performance value individual attributes represents \( i \)-th alternative for the \( j \)-th attributes.

After setting up the decision matrix, it is normalized using the procedure stated in Eq. (2).

\[
r_{ij} = \frac{X_{ij}}{\sum_{j=1}^{m} X_{ij}},
\]

where, \( r_{ij} \) is the normalized decision matrix.
The matrix is normalized by getting the ratio of each matrix value and the sum of matrix values of the column on which they belong.

Furthermore, the entropy value $e_{ij}$ is calculated using Eq. (3).

$$e_{ij} = -h \sum_{i=1}^{m} r_{ij} \ln r_{ij},$$

where $i = 1, 2, \ldots, m; j = 1, 2, \ldots, n; h = \frac{1}{\ln(m)}$; $m$ is the number of alternatives.

Finally, the weight vectors $w_{ij}$ are evaluated using the below-stated expression in Eq. (4).

$$w_{ij} = \frac{1 - e_j}{\sum_{i=1}^{m} (1 - e_j)},$$

where $j = 1, 2, \ldots, n$.

The quantity $d_j = 1 - e_j$ is known as degree of diversification.

### 2.2.3. TOPSIS Analysis and Selection of Priority List

The appropriateness of the method for normalization of the decision matrix values should show in making all the attribute values to be of the same dimensionality [1]. This normalization process is carried out using Eq. (5).

$$\bar{X}_{ij} = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{m} x_{ij}^2}}.$$ (5)

Next, the normalized performance values are weighted using Eq. (6).

$$\bar{V}_{ij} = w_{ij} \cdot \bar{X}_{ij},$$ (6)

For each alternative, values are selected that are closest to the ideal best and ideal worst of the system under consideration. The Euclidean distance from the ideal best and ideal worst values are calculated using Eqs. (7) and (8), respectively.

$$S_j^+ = \left[ \sum_{j=1}^{n} (V_{ij} - V_j^+) \right]^{0.5},$$

$$S_j^- = \left[ \sum_{j=1}^{n} (V_{ij} - V_j^-) \right]^{0.5}. $$

The performance score $P_i$ is calculated using Eq. (9).

$$P_i = \frac{S_j^-}{S_j^+ + S_j^-},$$

The performance score is an indication of a closeness to the ideal solution, it is within an interval of $\{0, 1\}$, the value closest to 1 represents the ideal best solution while the value closest 0 represents the ideal worst solution. The TOPSIS method is a multicriteria decision-making model with target-based criteria which makes it suitable for this work.
3. RESULTS AND DISCUSSION

The data table of the various iron-based additives and their attributes for model analysis and ranking of alternatives for enhanced anaerobic digestion of sludge are presented in Table 1. The selection of alternatives was restricted to literature information on efficiency, availability and frequency of use for anaerobic digestion of sludge. The additive costs used were average prices from reputable online stores. The six attributes were selected because their performances influence the choice of iron-based additives.

TABLE 1. SELECTED ATTRIBUTES FOR IRON-BASED ADDITIVES

| Additive types                 | VS removed, % | COD removal, % | VFA reduced, % | Biogas increase, % | Dosage, g/L | Cost, $  | VS removed, % |
|--------------------------------|--------------|----------------|----------------|-------------------|-------------|----------|--------------|
| Fe₂O₃                          | 40.00        | 52.40          | 60.00          | 35.52             | 20.00       | 36.176   | [30]         |
| Fe₂O₃ NPs                      | 45.00        | 90.90          | 95.52          | 35.00             | 0.75        | 1.3566   | [31]         |
| Fe₂O₃-10g/L                    | 47.40        | 45.70          | 40.00          | 29.90             | 10.00       | 243.95   | [18]         |
| Fe₂O₃ NPs-20                   | 49.88        | 52.54          | 90.00          | 73.90             | 0.02        | 0.0628   | [32]         |
| Fe₂O₃ NPs-100                  | 46.90        | 76.90          | 49.00          | 58.70             | 0.10        | 0.6521   | [17]         |
| Fenton Process (FeSO₄.7H₂O)    | 54.80        | 52.50          | 90.50          | 20.95             | 2.00        | 6.6319   | [33]         |
| Fe Powder                      | 49.60        | 66.20          | 70.00          | 40.80             | 5.00        | 0.6248   | [34]         |
| nZVI-1g/L                      | 23.80        | 86.60          | 80.00          | 58.44             | 1.00        | 18.207   | [35]         |
| nZVI-6g/L                      | 19.60        | 60.80          | 91.00          | 57.42             | 6.00        | 109.456  | [36]         |
| Trace Fe                       | 38.47        | 42.49          | 51.36          | 31.97             | 0.20        | 2.1468   | [37]         |
| WIS                            | 13.20        | 45.00          | 95.90          | 21.40             | 10.00       | 0.0032   | [38]         |
| ZVI                            | 42.40        | 37.00          | 88.80          | 91.50             | 10.00       | 0.8830   | [19]         |
| ZVSI                           | 52.60        | 52.90          | 62.40          | 38.30             | 1.00        | 0.0003   | [39]         |

The information in Table 1 was used for decision matrix development using Eq. (1). The matrix has column-wise attribute values and corresponding values of alternative (row-wise). In this study, a 13·6 decision matrix was formed.

However, matrix normalization for weight determination was carried out based on Eq. (2), the normalized matrix result is presented in Table 2.

TABLE 2. NORMALIZED MATRIX TABLE WITH ATTRIBUTES

| Additive types                 | VS removed, % | COD removal, % | VFA reduced, % | Biogas increase, % | Dosage, g/L | Cost, $  |
|--------------------------------|--------------|----------------|----------------|-------------------|-------------|----------|
| Fe₂O₃                          | 0.0759       | 0.0695         | 0.0622         | 0.0554            | 0.3027      | 0.0861   |
| Fe₂O₃ NPs                      | 0.0853       | 0.1206         | 0.0990         | 0.0546            | 0.0114      | 0.0032   |
| Fe₂O₃-10g/L                    | 0.0899       | 0.0606         | 0.0415         | 0.0466            | 0.1514      | 0.5806   |
| Fe₂O₃ NPs-20                   | 0.0946       | 0.0697         | 0.0933         | 0.1152            | 0.0003      | 0.0002   |
| Fe₂O₃ NPs-100                  | 0.0889       | 0.1020         | 0.0508         | 0.0915            | 0.0015      | 0.0016   |
| Fenton Process (FeSO₄.7H₂O)    | 0.1039       | 0.0696         | 0.0938         | 0.0327            | 0.0303      | 0.0158   |
| Fe Powder                      | 0.0941       | 0.0878         | 0.0726         | 0.0636            | 0.0757      | 0.0015   |
Again, the entropy values $e_{ij}$ were calculated based on Eq. (3) and Eq. (4) was used to compute the weight values $w_{ij}$. The results of entropy, degree of diversification and weight vectors were tabulated as shown in Table 3.

**TABLE 3. NORMALIZED DECISION TABLE WITH ENTROPY GENERATION**

| Additive types                          | VS removed, % | COD removal, % | VFA reduced, % | Biogas increase, % | Dosage, g/L | Cost, $ |
|----------------------------------------|---------------|----------------|---------------|--------------------|-------------|---------|
| Fe$_2$O$_3$                            | -0.1956       | -0.1853        | -0.1728       | -0.1602            | -0.3617     | -0.2111 |
| Fe$_2$O$_3$ NPs                        | -0.2100       | -0.2551        | -0.2290       | -0.1587            | -0.0508     | -0.0185 |
| Fe$_3$O$_4$-10 g/L                     | -0.2166       | -0.1699        | -0.1320       | -0.1429            | -0.2858     | -0.3156 |
| Fe$_3$O$_4$ NPs-20                     | -0.2231       | -0.1856        | -0.2213       | -0.2490            | -0.0025     | -0.0013 |
| Fe$_3$O$_4$ NPs-100                    | -0.2152       | -0.2328        | -0.1514       | -0.2188            | -0.0098     | -0.0100 |
| Fenton Process (FeSO$_4$.7H$_2$O)       | -0.2353       | -0.1855        | -0.2220       | -0.1118            | -0.1059     | -0.0655 |
| Fe Powder                              | -0.2223       | -0.2136        | -0.1904       | -0.1752            | -0.1953     | -0.0097 |
| nZVI-1 g/L                             | -0.1398       | -0.2486        | -0.2065       | -0.2183            | -0.0634     | -0.1360 |
| nZVI-6 g/L                             | -0.1224       | -0.2030        | -0.2227       | -0.2160            | -0.2179     | -0.3504 |
| Trace Fe                               | -0.2020       | -0.1412        | -0.1562       | -0.2590            | -0.0176     | -0.0267 |
| WIS                                    | -0.0923       | -0.1682        | -0.2295       | -0.1134            | -0.2858     | -9E–05  |
| ZVI                                    | -0.2027       | -0.1479        | -0.2196       | -0.2778            | -0.2858     | -0.0129 |
| ZVSI                                   | -0.2299       | -0.1864        | -0.1771       | -0.1683            | -0.0634     | -1.1E–05|
| $e_{ij}$                                | 0.9775        | 0.9837         | 0.9866        | 0.9628             | 0.7586      | 0.4516  |
| $d$                                    | 0.0225        | 0.0163         | 0.0134        | 0.0373             | 0.2414      | 0.5484  |
| $W_{ij}$                               | 0.0256        | 0.0185         | 0.0153        | 0.0424             | 0.2746      | 0.6237  |

It could be observed that most of the attributes showed low entropy value, according to Oluah et al. [23] may be due to the minimal difference between each value. Additive cost and dosage had the highest entropy value, this agrees with the views of Abdelsalam et al. [11] that additive price is a major choice in deciding the type of iron-based additive to be used for enhancing anaerobic digestion. Similarly, Ugwu et al. [26] reported that dosage had a major influence on the overall enhancement process, hence a deciding factor in the choice of alternatives. It is safe to say that in selecting iron-based additives for enhancement of anaerobic digestion, low dosage requirement and low cost of additives is of great importance.

The entropy weights assigned to each of the attributes were used in the TOPSIS analysis. The normalized decision matrix table was calculated with Eq. (5) and the result of the analysis was presented in Table 4.
### Table 4. Results of Normalized TOPSIS Analysis

| Additive types | VS removed, % | COD removal, % | VFA reduced, % | Biogas increase, % | Dosage, g/L | Cost, $ |
|----------------|---------------|----------------|----------------|-------------------|------------|--------|
| Fe₂O₃          | 0.2610        | 0.2405         | 0.2173         | 0.1829            | 0.7219     | 0.1337 |
| Fe₂O₃ NPs      | 0.2936        | 0.4171         | 0.3460         | 0.1802            | 0.0271     | 0.0050 |
| Fe₂O₃·10g/L    | 0.3093        | 0.2097         | 0.1449         | 0.1539            | 0.3609     | 0.9018 |
| Fe₂O₃ NPs-20   | 0.3255        | 0.2411         | 0.3260         | 0.3804            | 0.0007     | 0.0002 |
| Fe₂O₃ NPs-100  | 0.3060        | 0.3529         | 0.1775         | 0.3022            | 0.0036     | 0.0024 |
| Fenton Process (FeSO₄·7H₂O) | 0.3576      | 0.2409         | 0.3278         | 0.1079            | 0.0722     | 0.0245 |
| Fe Powder      | 0.3236        | 0.3038         | 0.2536         | 0.2100            | 0.1805     | 0.0023 |
| nZVI-1g/L      | 0.1553        | 0.3974         | 0.2898         | 0.3008            | 0.0361     | 0.0673 |
| nZVI-6g/L      | 0.1279        | 0.2790         | 0.3296         | 0.2956            | 0.2166     | 0.4046 |
| Trace Fe       | 0.2751        | 0.1585         | 0.1861         | 0.40982           | 0.0072     | 0.0079 |
| WIS            | 0.0861        | 0.2065         | 0.3474         | 0.1102            | 0.3609     | 1.19E–05 |
| ZVI            | 0.2767        | 0.1698         | 0.3217         | 0.4710            | 0.3609     | 0.0033 |
| ZVSI           | 0.3432        | 0.2428         | 0.2260         | 0.1972            | 0.0361     | 1.19E–06 |

The assigned weight to each attribute from the entropy analysis was used to calculate the weighted normalized TOPSIS table. This weighted normalization process was conducted with Eq. (6) and the resulting matrix table is shown in Table 5.

### Table 5. Weighted Normalized TOPSIS Table

| Additive types | VS removed, % | COD removal, % | VFA reduced, % | Biogas increase, % | Dosage, g/L | Cost, $ |
|----------------|---------------|----------------|----------------|-------------------|------------|--------|
| Fe₂O₃          | 0.0067        | 0.0044         | 0.0033         | 0.0078            | 0.1982     | 0.0834 |
| Fe₂O₃ NPs      | 0.0075        | 0.0077         | 0.0053         | 0.0076            | 0.0074     | 0.0031 |
| Fe₂O₃·10g/L    | 0.0079        | 0.0039         | 0.0022         | 0.0065            | 0.0991     | 0.5624 |
| Fe₂O₃ NPs-20   | 0.0083        | 0.0045         | 0.0050         | 0.0161            | 0.0002     | 0.0002 |
| Fe₂O₃ NPs-100  | 0.0078        | 0.0065         | 0.0027         | 0.0128            | 0.0010     | 0.0015 |
| Fenton Process (FeSO₄·7H₂O) | 0.0091      | 0.0045         | 0.0050         | 0.0046            | 0.0198     | 0.0153 |
| Fe Powder      | 0.0083        | 0.0056         | 0.0039         | 0.0089            | 0.0496     | 0.0014 |
| nZVI-1g/L      | 0.0040        | 0.0074         | 0.0044         | 0.0127            | 0.0099     | 0.0420 |
| nZVI-6g/L      | 0.0033        | 0.0052         | 0.0050         | 0.0125            | 0.0595     | 0.2524 |
| Trace Fe       | 0.0071        | 0.0029         | 0.0028         | 0.0174            | 0.0020     | 0.0050 |
| WIS            | 0.0022        | 0.0038         | 0.0053         | 0.0047            | 0.0991     | 7.41E–06 |
| ZVI            | 0.0071        | 0.0031         | 0.0049         | 0.0200            | 0.0991     | 0.0020 |
| ZVSI           | 0.0088        | 0.0045         | 0.0035         | 0.0084            | 0.0099     | 7.41E–07 |

Thereafter, the ideal best solution (V⁺) and ideal worst solution (V⁻) was calculated and presented in the last two rows of Table 6. The values were computed from the weighted normalized values by determining each attribute’s highest values and lowest values. Since the
achievement of cost minimization and low dosage input is of great interest in this study, the lowest values were regarded as the ideal best solution and the highest values were the ideal worst solution [29].

The separate measure for each alternative was determined from the Euclidean distance between the alternative and its specific ideal solution. Both positive and negative separation measures for each alternative were calculated with Eq. (7) and Eq. (8) and presented in Table 6.

| Additive types         | VS removed, % | COD removal, % | VFA reduced, % | Biogas increase, % | Dosage, g/L | Cost, $ | S+   | S–   |
|------------------------|---------------|----------------|----------------|-------------------|--------------|---------|------|------|
| Fe₂O₃                  | 0.0067        | 0.0044         | 0.0033         | 0.0078            | 0.1982       | 0.0834  | 0.2153 | 0.4791 |
| Fe₂O₃ NPs              | 0.0075        | 0.0077         | 0.0053         | 0.0076            | 0.0074       | 0.0031  | 0.0148 | 0.5910 |
| Fe₂O₃ 10g/L            | 0.0079        | 0.0039         | 0.0022         | 0.0065            | 0.0991       | 0.5624  | 0.5712 | 0.0993 |
| Fe₂O₃ NPs-20           | 0.0083        | 0.0045         | 0.0050         | 0.0161            | 0.0002       | 0.0002  | 0.0051 | 0.5963 |
| Fe₂O₃ NPs-100          | 0.0078        | 0.0065         | 0.0027         | 0.0128            | 0.0010       | 0.0015  | 0.0080 | 0.5947 |
| Fenton Process (FeSO₄·7H₂O) | 0.0092      | 0.0045         | 0.0050         | 0.0046            | 0.0198       | 0.0153  | 0.0294 | 0.5755 |
| Fe Powder              | 0.0083        | 0.0056         | 0.0039         | 0.0089            | 0.0496       | 0.0014  | 0.0507 | 0.5804 |
| nZVI-1g/L              | 0.0040        | 0.0074         | 0.0044         | 0.0127            | 0.0099       | 0.0420  | 0.0440 | 0.5536 |
| nZVI-6g/L              | 0.0033        | 0.0052         | 0.0050         | 0.0125            | 0.0595       | 0.2524  | 0.2594 | 0.3398 |
| Trace Fe               | 0.0071        | 0.0029         | 0.0028         | 0.0174            | 0.0020       | 0.0050  | 0.0082 | 0.5912 |
| WIS                    | 0.0022        | 0.0038         | 0.0053         | 0.0047            | 0.0991       | 7.41E-06 | 0.1004 | 0.5711 |
| ZVI                    | 0.0071        | 0.0031         | 0.0049         | 0.0200            | 0.0991       | 0.0020  | 0.0991 | 0.5693 |
| ZVSI                   | 0.0088        | 0.0045         | 0.0035         | 0.0084            | 0.0099       | 7.41E-07 | 0.0156 | 0.5932 |
| V+                     | 0.0091        | 0.0077         | 0.0053         | 0.0200            | 0.0002       | 7.41E-07 | 0.1982 | 0.5624 |
| V–                     | 0.0022        | 0.0029         | 0.0022         | 0.0046            | 0.1982       | 0.5624  | 0.5624 | 0.5624 |

The relationship between the Euclidean distances from the ideal best and worst solutions for iron-based additive alternatives was depicted by a comparative plot presented in Fig. 2. The complementary nature of the Euclidean distances as shown in Fig. 2 indicates the mathematical operations were accurately implemented [23]. It could be observed from the comparative plot that the performance of Fe₃O₄ NPs-20 and Fe₃O₄ NPs-100 had the shortest Euclidean distance from the ideal best solution and the widest Euclidean distance from the ideal worst solution. This according to Vannarath and Thalla [1] and Zhu et al. [29] show that Fe₃O₄ NPs-20 with the shortest distance is had the best performance among other alternatives.

Finally, the ranking of iron-based additives was based on the decrease in the suitability index value. Therefore, the alternative (Fe₃O₄ NPs-20) with a performance score (highest TOPSIS score) closest to 1 was chosen as the best enhancement method. This choice also represents the ideal best solution (with the least Euclidean distance), it was presented in Table 7 together with the separation measures. The ranking with the performance scores as seen in Table 7 also agrees with the plot of Euclidean distances of idea best and worst solution.

The ranking of conductive iron oxide like Fe₃O₄ NPs-20 as the best alternative agrees with previous studies due to its ability to stimulate the growth of methanogens, promote the direct
interspecies transfer of electron in syntrophic methane production, improvement of substrate solubilization, etc. [14], [18].

![Comparative plot of Euclidean distances from the ideal solutions.](image)

**Fig. 2.** Comparative plot of Euclidean distances from the ideal solutions.

**TABLE 7. POSITIVE AND NEGATIVE SEPARATION MEASURES, TOPSIS SCORES AND RANKING OF ALTERNATIVES**

| Additive types               | $S^+$ | $S^-$ | $P_i$  | Rank |
|------------------------------|-------|-------|--------|------|
| Fe$_2$O$_3$                  | 0.2153| 0.4791| 0.6900 | 11   |
| Fe$_2$O$_3$ NPs              | 0.0147| 0.5910| 0.9757 | 4    |
| Fe$_3$O$_4$-10g/L            | 0.5712| 0.0993| 0.1481 | 13   |
| Fe$_3$O$_4$ NPs-20           | 0.0051| 0.5963| 0.9915 | 1    |
| Fe$_3$O$_4$ NPs-100          | 0.0080| 0.5947| 0.9867 | 2    |
| Fenton Process (FeSO$_4$.7H$_2$O) | 0.0294| 0.5755| 0.9514 | 6    |
| Fe Powder                    | 0.0507| 0.5804| 0.9197 | 8    |
| nZVI-1g/L                    | 0.0440| 0.5536| 0.9264 | 7    |
| nZVI-6g/L                    | 0.2594| 0.3398| 0.5671 | 12   |
| Trace Fe                     | 0.0082| 0.5912| 0.9863 | 3    |
| WIS                          | 0.1004| 0.5711| 0.8505 | 10   |
| ZVI                          | 0.0991| 0.5693| 0.8518 | 9    |
| ZVSI                         | 0.0156| 0.5932| 0.9744 | 5    |
Similarly, amongst other additives studied in Abdelsalam et al. [40], it was shown that the use of 20 mg/L Fe$_3$O$_4$ NPs (Fe$_3$O$_4$ NPs-20) achieved the highest biogas yield of 584 mL/gVS from the enhanced anaerobic digestion. Casals et al. [15] also reported a 180 % rise in biogas production after supplementation of anaerobic digestion with Fe$_3$O$_4$ NPs.

4. **CONCLUSION**

Enhancement of anaerobic digestion is indispensable due to the limited availability of conventional feedstocks, recalcitrancy to biodegradation by the available substrates, presences of inhibitors or nutrient deficiency, etc. The selection of such appropriate enhancement for anaerobic digestion of sludges is a herculean task. In this study, the selected enhancement option (iron-based additives) was ranked using the MADM technique for the selection of the best from alternatives. The TOPSIS method and weight determination via entropy weight approach were implemented for the selection of the most suitable iron-based additive from thirteen (13) alternatives and six (6) attributes. Using the entropy method, weights were assigned to pertinent attributes (from many possible attributes) and the alternatives were ranked via the TOPSIS technique based on the performance scores (between 0,1). The result showed that additive cost and dosages were assigned the highest weight of 62.37 % and 27.46 %, respectively. Based on the performance scores of 99.15 %, 20 mg/L of Fe$_3$O$_4$ nanoparticles (Fe$_3$O$_4$ NPs-20) ranked best (number 1) among considered alternatives for enhancement of anaerobic digestion of sludge. It was concluded that Fe$_3$O$_4$ NPs-20 with the closest score to 1 and the least Euclidean distance from the ideal best solution was selected as the best alternative (iron-based additive is most suited for enhanced anaerobic digestion of sludges for best performance. It was noteworthy that the MADM technique works well in ranking the iron-based enhancement of anaerobic digestion of sludges.

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