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Maximizing bio-methane potential from municipal landfill leachate through ultrasonic pretreatment

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A R T I C L E I N F O

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A B S T R A C T

In the quest for sustainable waste management solutions, this study explores the integration of ultrasonic pretreatment as a preparatory step for the anaerobic digestion of landfill leachate. Employing response surface methodology (RSM) coupled with central composite design (CCD), we systematically optimize the process parameters, including pH, inoculum volume, and ultrasonic pretreatment duration, to maximize the yield of bio-methane potential (ml CH_4/g VS). The results demonstrate the effective application of RSM-CCD for predicting and modelling methane generation, with a highly significant model (R^2 = 0.899). The optimized conditions reveal a remarkable biomethane potential of 177 ml CH_4/g VS. Additionally, this study contributes to the understanding of the positive effect of ultrasound pretreatment on the anaerobic digestion of landfill leachate, and the quality of the digestate obtained after anaerobic digestion was studied and different valorisations were proposed.

1. Introduction

In previous decades, the growth in population and changing consumption patterns have increased the production of waste around the world. Landfills have been used as quick and economical alternatives for governments to manage their household waste. Nonetheless, their exploitation has impacts on the environment, such as the requirement of large areas of land, emissions of gaseous pollutants (H_2S, CH_4), and the generation of large volumes of leachate [1]. Leachate generated by the waste remains one of the most difficult pollutants to treat, it is defined as the water that percolates through the landfill waste that is loaded bacteriologically and chemically by mineral and organic substances, their composition depends mainly on the source of the landfill content and the quantity of precipitation, and the age of the landfill [2,3]. A number of different treatment approaches have been applied for leachate processing, various natural treatment methods such as coagulation and flocculation, infiltration percolation, advanced oxidation processes (AOP), nitrification and denitrification, and anaerobic digestion [4–7].

Faced with the scarcity of nonrenewable resources and the necessity to diminish greenhouse gas (GHG) emissions, the energy transition through the circular economy is essential. Anaerobic digestion is fully in line with this approach and remains a promising alternative with multiple benefits for organic waste management [8]. It is used to minimize pollution by reducing organic matter, and to generate biogas as a renewable energy which may be exploited by providing electricity heat for individuals and companies, or on-site by cogeneration. In landfill leachate, however, due to the different contaminants present and their higher concentrations, single

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treatment methods are not effective [9]. It is possible to achieve higher treatment efficiency by using a coupled method that has a possible synergistic effect. For example, the combined effects of synergistic processes of persulfate and hydrogen peroxide activated by microwave radiation have enhanced the treatment of landfill leachate [10]. In many investigations, multiple treatments in series were employed to enhance the treatment efficacy [9,11,12].

In the last few years, ultrasonic treatment was identified as showing promise for the treatment of water [13], sludge [14], industrial wastewater [15], manure [16], and for different applications [17,18]. Ultrasound is usually used as an adjunct to conventional treatment processes for pre-treatment or post-treatment because the time and power required to achieve total mineralization/solubilization of contaminants are not practical. Deepanraj et al. showed that ultrasonically treated food waste has greater biogas generation than microwave and autoclave treatment [19]. Ultrasonics, as an advanced oxidation process with physico-chemical reactions, has a great capacity to decompose organic and non-organic constituents contaminated liquid media such as wastewater and leachate. In generally, the intensification of the process by sonication is ascribed to the cavitation phenomenon. Cavitation describes the formation and radial oscillation of gas and vapor bubbles in a liquid under the effect of the pressure change generated by the propagation of an ultrasonic wave. The cavitation transient creates an intense concentration of energy on an extremely short temporal and spatial scale. Therefore, sonication is a single tool to insert energy into the reaction system to induce the desired chemical-physical-biological changes [20]. As a part of the pre-treatment of leachate to support its anaerobic digestion, ultrasound has many benefits impacts like the breakdown of organic macromolecules into small molecules, that may be rapidly digested by the micro-organism cells leading in a higher generation of biomethane [21,22].

Compared to other pretreatment methods [23], ultrasound is a relatively low-cost and energy-efficient technology that can be easily retrofitted into existing systems. It has been shown to be effective in increasing biogas production from a variety of feedstocks, including agricultural waste, lignocellulosic materials, and sewage effluent. However, the economic success of ultrasound pretreatment will depend on a variety of parameters unique to each system, and further research is needed to fully understand its impact on feedstock disintegration and microbial communities. Karouach et al. showed that ultrasonic pretreatment of Anaerobic fermentation of organic waste fraction for 24 min improves the methane production and then substrate degradation respectively by 29 % and 14 % [24]. The research carried out by Huacheng Xu et al. on anaerobic digestion of sludge using reactors with a total volume of 4.0 L in mesophilic conditions, show that the pre-treatment with ultrasound increases the efficiency of anaerobic digestion by 7–8% [25]. Moreover, a research study done by Matia Mainardis et al. on Cheese whey showed that the ultrasound treatment increased the methane yield by (+16 %) compared to unsonicated cheese whey [26]. As mentioned, different studies have shown the advantages of ultrasonic pretreatment during anaerobic digestion of different organic wastes, such as household organic waste fraction, dairy waste, and sludges.

Within the same context, the amount of methane generated by anaerobic digestion of organic waste depends on several parameters such as pH, C/N ratio, temperature, substrate concentration, percentage of inoculum etc. Several researchers have studied the influence of anaerobic digestion factors on methane generation. Deepanraj et al. explored the influence of temperature (30–60 °C), pH (5–9), codigestion (0–40 % poultry manure), and solids concentration (5–15 %) on chemical oxygen demand (COD) degradation and biogas generation from anaerobic digestion of food waste using CCD-RSM, they detailed that the optimal conditions obtained were a solid concentration of 7.38 %, pH value as 7, temperature at 48.43 °C, and co-digestion as 29 % produce a maximum biogas of 6344 ml and a COD degradation of 38 % [27]. S. Lhanafi et al. investigated the evaluation of bio-methane potential (L CH_4/Kg VS) of dairy wastes as a function of three factors (organic load, inoculum, and pH) by using Factorial design and they reported that the optimal conditions selected after the execution of the model are pH 8 and IN_1 as inoculum with a divergence was seen for organic charge. The optimal conditions with the use of 3.44 g VS as organic charge showed a reduction of 89 % in volatile solids [28].

In the current study, the objective is to examine the integration of the ultrasonic process for leachate as a pretreatment before anaerobic digestion. The RSM based on CCD was used to optimize the process parameters for potential bio-methane production, the three parameters that were studied are (pH value, inoculum volume, ultrasonic pretreatment), with each parameter in the plan was investigated at five different levels (-α, −1, 0, +1, +α). The main effect of each individual factor and the interaction effect between individual factors were also studied.

Fig. 1. Tamellast landfill site.

2. Materials and methods

2.1. Feedstock

The landfill leachate applied in this study was taken from the municipal solid waste landfill of Tamellast in Agadir city, Morocco (Fig. 1). The landfill is operated since 2010 with a area of 41 ha, intended to receive the controlled landfill of Agadir is located about 6 km as the crow flies northeast of Agadir at Lambert coordinates (X: 104 182 - 105 182, Y: 388 640 - 389 926), and received approximately 300 000 tons of waste per year. Once the in-situ parameters were measured, the leachate was pooled into 10 L capacity plastic bottles, filtered to remove greater suspended solids, and kept at 4 °C in the laboratory until use. The physical and chemical characterization of landfill leachate was given in Table 1.

2.2. Inoculum collection and acclimatization

The inoculum most generally recommended is the digestate from anaerobic sewage treatment plants, because of the diversity and activity of the microorganisms it contains [29,30]. Sewage plant sludge was used as inoculum for the methanization of leachate. The sludge was obtained in an anaerobic decanter of the M'Zar wastewater treatment plant in Agadir, Morocco.

The sludge was moistened and sieved before being diluted in distilled water and activated with a synthetic solution of lactic acid, sodium acetate, and glucose (GAL solution). And with mineral water with the following characteristics, (potassium 3 mg/L, sulfates 42 mg/L, sodium 26 mg/L, calcium 12 mg/L, magnesium 9 mg/L, bicarbonates 104 mg/L, and chlorides 14). All this was added as a source of nutrients, to form the inoculum used in the inoculation of the digesters, and the characterization of the prepared inoculum was shown in Table 1. Finally, the inoculum was acclimated for 12 days at 38 °C before use [31].

2.3. Protocol for ultrasound pretreatment of leachate

Ultrasound pretreatment in anaerobic digestion can enhance microbial cell disruption, promote mass transfer, increase organic solubilization, stimulate microbial activity, and improve digestate quality [21,32,33]. These electrical effects result in improved methane production rates and process efficiency [34].

Leachate pre-treatment was carried out using an ultrasound bath. Different ultrasonication durations of 0–100 min were applied to the sample leachate in a glass dark bottle of 300 ml volume using ultrasound (SB-100DT Ultrasonic Cleaner). The placement of the vials in the ultrasonic bath was precisely controlled, and the temperature of the samples was controlled with a thermometer and monitored by circulating cooling water around the vials to maintain an ambient temperature of 25 °C at a frequency of 40 kHz. The selection of ultrasonic pretreatment conditions was based mainly on the literature.

2.3 Experimental set-up.

In this study the production of methane from leachate by anaerobic digestion was performed using batch reactors. The laboratory-scale reactors used are 500 ml digesters (with a liquid volume of 300 ml). The procedure is to load the digester with a mixture of inoculum and leachate and let them digest. which were maintained in mesophilic condition (38 °C) in a water bath containing water. The biogas produced was purified by a highly concentrated NaOH (6 N) solution for CO_2 removal, according to the following chemical reaction:

$$2\ NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

The volume of bio-methane produced is measured with the aid of the water displacement approach [31], The entire system is strictly controlled before the test to ensure the security of the whole closing system. The experiments have been replicated and the average of bio-methane production has been reported.

2.4. Analytical methods

The analyzed leachate parameters such as pH, Conductivity, total solids (TS), volatile solids (VS), chemical oxygen demand (COD) and biological Oxygen demand (BOD) were performed according to Standard Methods for Water and Wastewater Examination [35]. Digestate was analyzed by Fourier transform infrared (FTIR) by using SHIMADZU IRAffinity-1S in the frequency range of 400–4000

Table 1
Mean values of physicochemical parameters of inoculum and leachate.

Parameters	Unit	Inoculum	Landfill leachate
Conductivity	µS/cm	–	37,400
pH	–	6.93	8.11
BOD_5	mg O_2/l	–	1621
COD	mg O_2/l	–	5100
BOD_5/COD	–	–	0.32
Total solide (TS)	g/l	77.04	31.3
% VS from TS	%	57.65	48.88

cm^{-1}, and the morphology was characterized by scanning electron microscope (SEM) by using a JEOL JSM IT-100 microscope coupled to an EDS analyzer sensor to determine the quantitative elemental composition. All the parameters were carried out in the Materials and Environment Laboratory of Ibn Zohr University.

2.5. Experimental design and mathematical model

The process of anaerobic digestion in batch digesters is influenced by a wide variety of factors. In this study, we focus on three factors, pH, inoculum volume, and ultrasound pretreatment. The selected parameters were chosen based on a previous study investigating ultrasonic pretreatment on two types of leachates with a variation of inoculum percentage and pH [36]. Preliminary experiments indicated that landfill leachate performed better than truck leachate and ultrasound pretreatment had a positive impact on methane yield. Then, the selected factors have been studied and optimized by the methodology of the response surface (RSM) coupled to CCD.

- CCD-RSM design

RSM is an effective method for the design of experiments and optimization of various environmental processes [37,38]. It was employed in this study to optimize the yield of BMP from landfill leachate and to determine second-degree polynomial relationships between the input variables: pH (X_{pH}), volume of inoculum (X_{In}), and ultrasound pretreatment (X_{Pt}) that were selected after the preliminary test.

The effects of these factors were investigated using central composite design (CCD). Each parameter was investigated at five levels (-α, −1, 0, +1, +α) and are presented in Table 2, which produces a total of 20 experimental trials, including 6 axial points, 8 cube points and 6 central repetitive points. The cubic points help estimate the main and interaction effects, the axial points help estimate the quadratic effects, and the canter points help estimate the noise term [39].

Each experiment was repeated three times and the average was taken as the response Y [40]. In order to calculate the coefficients of the polynomial model, we used Eq. (1):

$$Y = \beta_0 + \sum \beta_i Xi + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j \quad (1)$$

where Y was the response variable, β_0 was the value for the fixed response at the central point of the experiment, β_i, $\beta_{ii,}$ and β_{ij} were the regression coefficients of the variables for the linear, quadratic, and interaction coefficient, respectively, and X_i and X_j represent the independent variables.

For more clarity, the methodology applied in this work was illustrated in Fig. 2.

3. Results and discussion

3.1. Experimental design and daily production

The central composite design (CCD) was introduced to investigate the effect of different factors (pH value, inoculum volume, ultrasonic pretreatment) in a mesophilic temperature on the biomethane potential (BMP) in order to determine the best conditions. These tests are performed directly after sampling to be as close as possible to reality. Table 3 shows the coded and actual levels of the factors employed in the design, and the results obtained after the design was executed.

According to the quadratic model equation, the selected responses are related to the tree independent parameters as follows (Eq. (2)):

$$\text{BMP (ml } CH_4\text{/g VS)} = 133.5 + 20.7\, X_{pH} + 7\, X_{PT} - 16\, X_{In} - 0.7 \times {}^2{}_{pH} - 3.9\, X^2{}_{PT} - 6.9\, X^2{}_{In} + 0\, X_{pH\text{-}PT} - 7\, X_{pH\text{-}In} - 2.5\, X_{PT\text{-}In} \quad (2)$$

For the validation of the model, analysis of variance (ANOVA) was utilized as a statistical analysis tool to test the significance of independent variables and their interactions. The results of Table 4 show that the p-value for the quadratic model is less than 0.05 (<0.01), which indicate the model was significant. In the following, the predicted R^2 value (0.899) and adjusted R^2 (0.807) values of the quadratic models for BMP are closely related to each other, with the difference between these parameters being less than 0.2, this proves the well correlation of the experimental and calculated data.

The significance of all variables the linear, quadratic, and interaction terms was evaluated by p-values (Table 4)**.** The terms having a p-value less than 5 % are said to be significant. Here the pH (X_{pH}), ultrasonic pretreatment (X_{PT}), inoculum (X_{In}) and their quadratic

Table 2
pH, Inoculum Volume, and Pretreatment Levels in Central Composite Design Experiments.

Factor	Symbol	Units	Level				
			−1.68	−1	0	+1	+1.68
pH	X_{pH}	–	5.3	6	7	8	8.7
Pretreatment	X_{PT}	min	0	20.4	50.4	80.4	100.9
Inoculum	X_{In}	ml	27.9	47	75	103	122

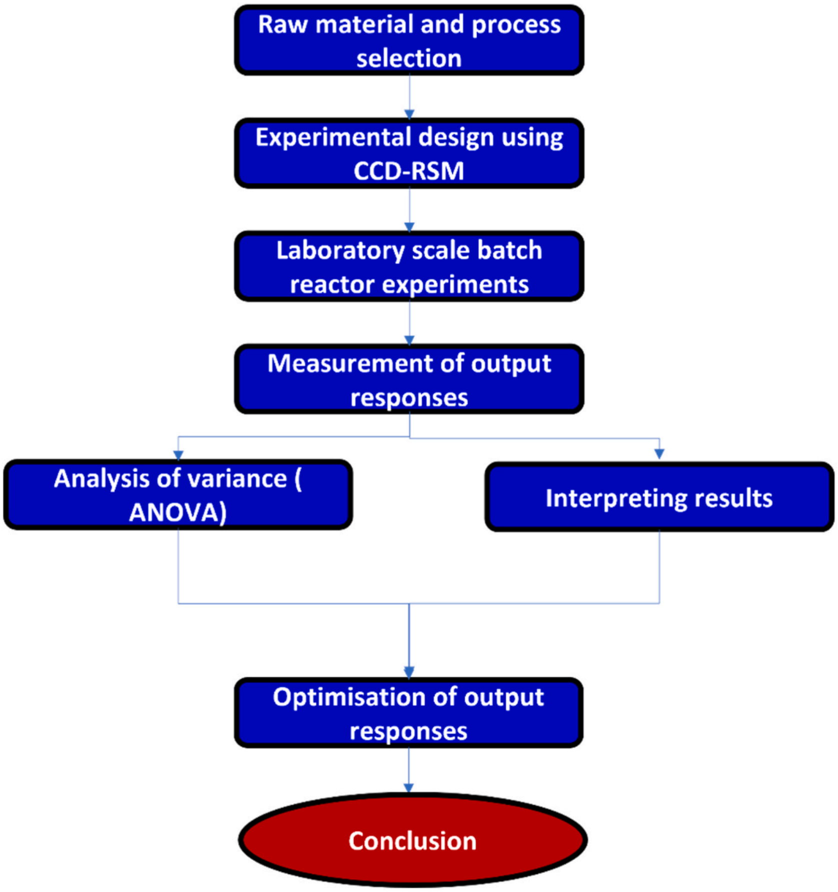


Fig. 2. Methodology used in this study.

Table 3
Levels of factors (coded and actual) and biomethane potential results.

Run	Coded values			Actual values			BMP (ml CH_4/g VS)				Variance
	X_1	X_2	X_3	X_1	X_2	X_3	Exp.1	Exp.2	Exp.3	Average	(σ^2)
1	−1	−1	−1	6	20.4	47	115	112	113	113	2.33
2	+1	−1	−1	8	20.4	47	162	169	168	166	14.33
3	−1	+1	−1	6	80.4	47	128	125	132	128	12.33
4	+1	+1	−1	8	80.4	47	179	187	182	183	16.33
5	−1	−1	+1	6	20.4	103	80	85	86	84	10.33
6	+1	−1	+1	8	20.4	103	111	109	113	111	4
7	−1	+1	+1	6	80.4	103	94	86	92	91	17.33
8	+1	+1	+1	8	80.4	103	115	115	118	116	3
9	-r	0	0	5.3	50.4	75	89	93	95	92	9.33
10	+r	0	0	8.7	50.4	75	163	164	167	165	4.33
11	0	-r	0	7	0	75	103	106	102	104	4.33
12	0	+r	0	7	100.9	75	135	132	138	135	9
13	0	0	-r	7	50.4	27.9	120	119	120	120	0.33
14	0	0	+r	7	50.4	122	102	104	99	102	6.33
15	0	0	0	7	50.4	75	136	130	131	132	10.33
16	0	0	0	7	50.4	75	134	130	130	132	5.33
17	0	0	0	7	50.4	75	133	138	139	137	10.33
18	0	0	0	7	50.4	75	130	127	134	130	12.33
19	0	0	0	7	50.4	75	134	136	133	134	2.33
20	0	0	0	7	50.4	75	140	134	138	137	9.33

Table 4
Analysis of variance (ANOVA) for anaerobic digestion of leachate.

Terms	Coefficient	t-value	*P*-value (%)
Model	–	–	<0.01
Constant	133.5	113.84	<0.01
X_1	20.7	26.61	<0.01
X_2	7.0	9.05	0.0275
X_3	−16.0	−20.54	<0.01
X_{1-1}	−0.7	−0.97	37.6
X_{2-2}	−3.9	−5.17	0.355
X_{3-3}	−6.9	−9.14	0.0263
X_{1-2}	0.0	0.00	100.0
X_{1-3}	−7.0	−6.89	0.0988
X_{2-3}	−2.5	−2.46	5.7
Lack of fit	–	–	0.01
R^2	0.899	–	–
R^2_{Adj}	0.807	–	–

terms (X^2_{PT} and X^2_{In}) to which was added tree interaction term (X_{pH-In}) have p-value less than 5 % and hence selected as significant model terms. And the factors which have a *P*-value of more than 5 % will be eliminated from Eq. (2). Therefore, Eq. (3) was developed by deleting the insignificant terms from Eq. (2).

$$BMP\ (ml\ CH_4/g\ VS) = 133.5 + 20.7\ X_{pH} + 7\ X_{PT} - 16\ X_{In} - 3.9\ X^2_{PT} - 6.9\ X^2_{In} - 7\ X_{pH\text{-}In} \quad (3)$$

In the end, the model postulated is confirmed and can be utilized for predicting responses in the experimental domain or for optimization, which has been given in Eq. (3).

Fig. 3a shows the values of the predicted against actual values for BMP. As can be understood from Fig. 3a, All the data points are either on or close to the Henry line, and therefore there is a good agreement between the experimental data and the predicted values for the response. On the other hand, Fig. 3b shows a graphic representation of the residues, it shows a homogeneous distribution on the zero axis. In light of all these results, we could conclude that the proposed mathematical model was suitable for the selected responses and appropriate for the analysis and optimization of bio-methane potential.

The daily production of methanogenic yields achieved through all the digesters was calculated via the water displacement method and shown in Fig. 4. It is clear that from Fig. 4 the methane generated in the digesters was divided into two phase profiles. In the first phase (I), the production of bio-methane potential (BMP) showed a rapid increase during the initial 48 h, is due to the high activity of hydrolytic and acidogenic bacteria. As these bacteria break down the organic material, they release large amounts of volatile fatty acids, which are then converted into methane and carbon dioxide by acetogenic and methanogenic bacteria. This results in a rapid increase in the production of methane, which means that the bacteria are well adapted to the substrate and that because the leachate from the landfill is at an advanced stage of the process of anaerobic digestion, it promotes and accelerates the production of methane. In the second phase (II), the rate of methane production slows down as the substrate becomes depleted and the activity of methanogenic bacteria becomes limited by nutrient availability. From the results, the highest bio-methane potential yield was obtained during experiment 4 under pH 8, 47 ml of inoculum, and 80,4 min of ultrasound pretreatment. while the lowest bio-methane potential yield was generated at experiment 5 with pH 6, 20.4 min of ultrasound pretreatment, and 103 ml of inoculum. Therefore, according to results of Table 3, the ultrasonic pretreatment and pH between 7 and 8.7 have a significant impact on BMP production. On the other hand, an excessive amount of inoculum compared to substrate could negatively affect methane production. Similar research conducted by Lili Yang et al. showed that adjusting the pH for methanization of food waste to pH 8 results in a maximal biomethane yield of 171.0

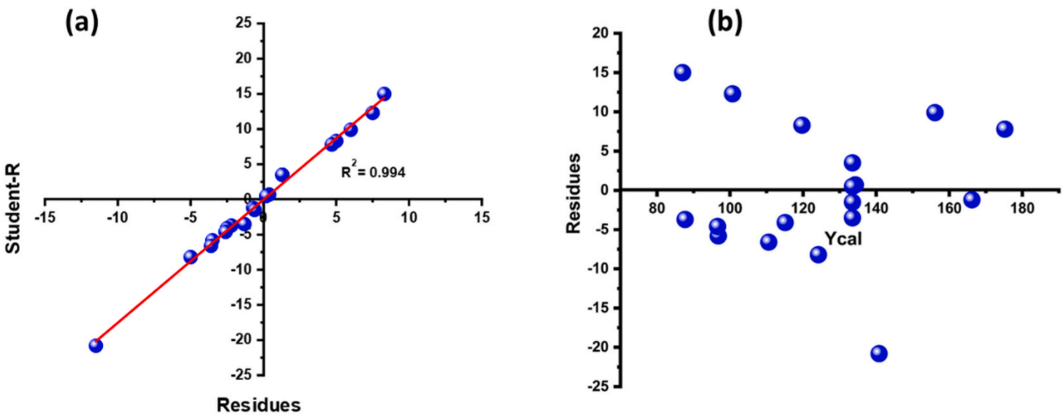


Fig. 3. (a) Plot of raw residuals versus case number. (b) Probability as a function of residual.

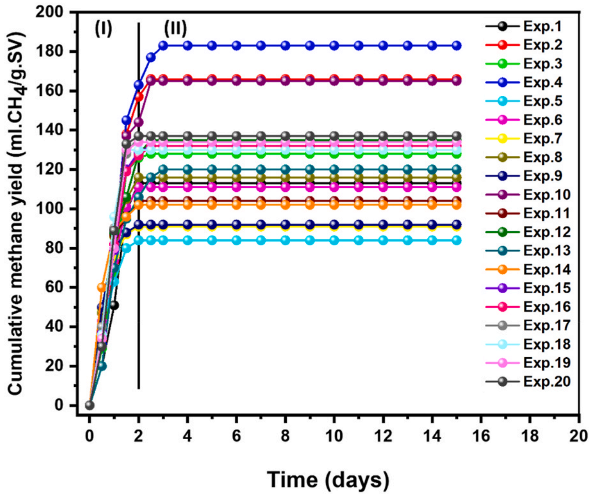


Fig. 4. Cumulative yield of bio-methane potential (BMP).

ml g^{-1} TS, that is 7.57 more compared to the unadjusted pH [41]. Another study was done by Jayaraj et al. examined how pH (5- 6- 7–8 and 9) affected generation of biogas from food waste in a batch digester with a 30-day retention period. The study results showed the maximum biogas yield was achieved at pH 7 with a production of 5655 L from a 2000 ml batch digestor [42]. On the other hand, concerning the pretreatment by ultrasound, Deepanraj et al. conducted anaerobic co-digestion trials in the thermophilic phase (50 °C) of food waste and poultry manure, according to the authors, the pre-treatment co-digested substrate containing 70 % of food waste and 30 % of poultry manure with ultrasonication produced approximately 10.12 % more biogas than the untreated substrate, which shows the importance of ultrasound treatment in improving the anaerobic digestion process [43].

3.2. Response surfaces

Plotting three-dimensional response surface graphs allowed us to study the interaction effects of the selected response (BMP), by keeping one variable at the central level of the plot and distinguishing the others within the chosen experimental interval. The two-dimensional and three-dimensional surface curves for relations between the independent parameters (pH, inoculum volume (ml), pre-treatment (min)) and the selected response are illustrated in Fig. 5.

Fig. 5a shows the interaction outcomes of pH and ultrasound pretreatment. From the plot of 3D, as seen, the cumulative bio-methane production (ml CH_4/g VS) increased with increasing pH from 5 to 8 and ultrasonic pretreatment from 0 min to 50 min. The ultrasonic pretreatment showed an improvement in cumulative methane production by 22.2 % yield in neutral pH compared to untreated. This can be explained by the strong microturbulence produced by ultrasonic waves, which leads to the decomposition and solubilization of the solids in suspension. Oxidizing radicals such as ·OH also induce hydrolysis of organic matter in suspended solids, making them more degradable [44]. The above results clearly show that cumulative methane production is highly affected by both pH and ultrasound pretreatment.

The effect of the interaction between pH and inoculum on methane production is displayed in Fig. 5b. It is clearly shown that cumulative methane production is highly affected by both pH and inoculum. The cumulative methane production was reduced by decreasing the value of pH and increasing the volume of inoculum, and it increases when the inoculum value is between 26 ml and 75 ml, and at the same time when the pH value increases to 8. The mechanism by which increasing inoculum volume and decreasing pH reduces cumulative methane production is likely due to the inhibition of methanogenic archaea by acidic conditions and competition with other microbial populations for limited resources, resulting in reduced system efficiency. When the volume of inoculum is within the optimal range (26 ml–75 ml), microbial population competition can be reduced, resulting in improved efficiency and increased methane production. This is because the optimal volume of inoculum can provide sufficient numbers of methanogenic bacteria to degrade the substrate and generate methane without being limited by competition from other microbial populations.

On the other hand, increasing the pH to 8 may increase the activity of methanogenic bacteria. This is due to the fact that methanogenic bacteria are more active in alkaline conditions and can tolerate higher pH levels than acidic conditions. In addition, an increase in pH can reduce the activity of other microbial populations, such as acidogenic bacteria, which may compete with methanogens for substrates. This decrease in competition can lead to an improvement in the efficiency of the system and consequently an increase in methane production.

The combined effect of pretreatment and inoculum on the cumulative methane production is given in Fig. 5c. As can be seen, methane production gradually increased when the pre-treatment time was increased from 0 to 102 min, as well as when the inoculum volume was increased from 26 to 75 ml (the optimal range). Overall, the increase in the generation of methane from landfill leachate with increasing ultrasound pre-treatment time and optimal inoculum volume (26 ml–75 ml) can be attributed to a combination of several parameters, such as enhanced solubilization and biodegradability of organic matter, sufficient numbers of active micro-

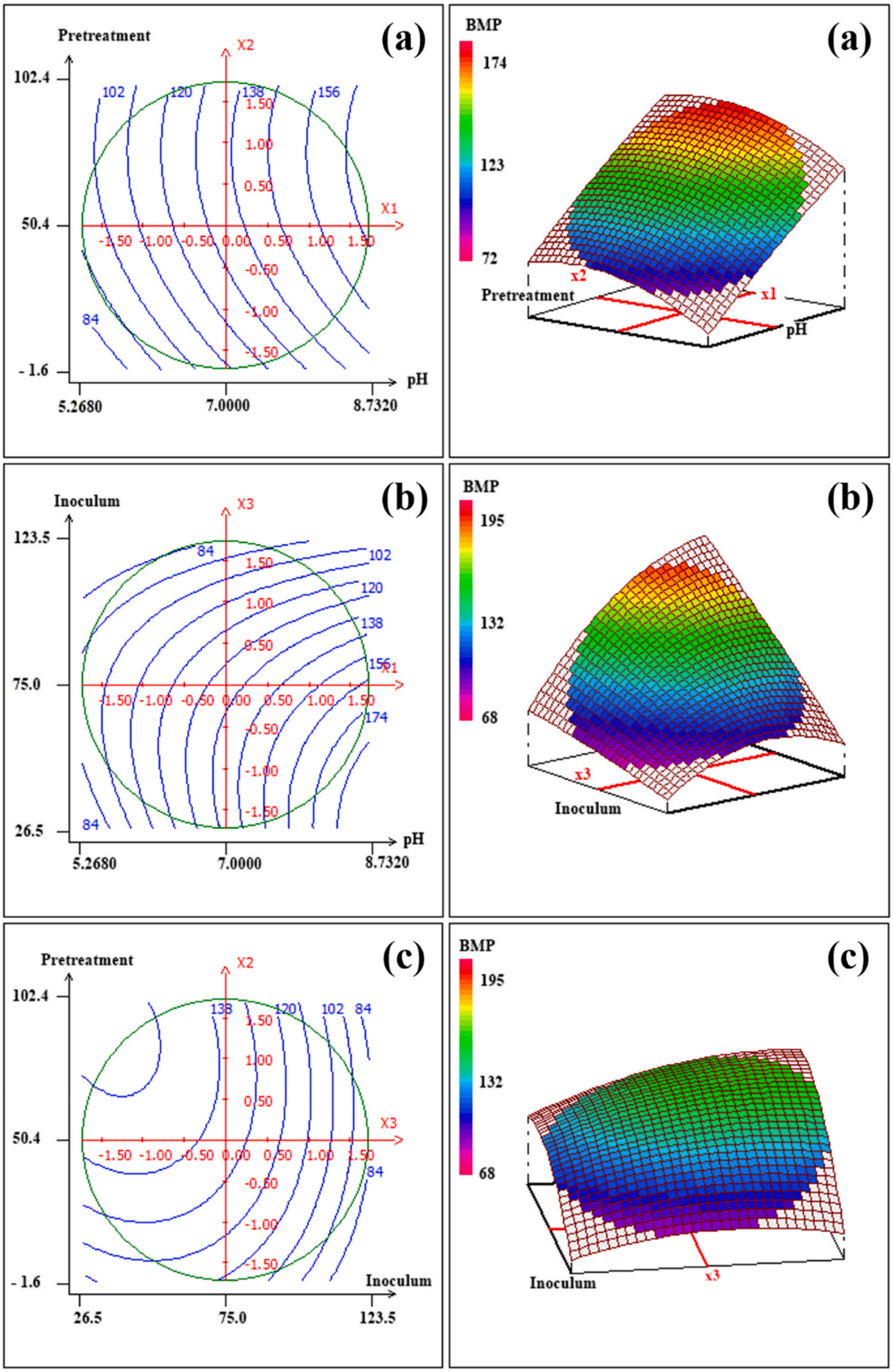


Fig. 5. 2D-3D surface plots of the effect of the interaction between pH and pretreatment (a), Inoculum and pH (b), and pretreatment and inoculum (c) on the cumulative yield of bio-methane potential (BMP).

organisms, stability and variety of the microbial community, nutrient availability, higher proportion of methanogenic microorganisms, and release of cellular components.

In order to evaluate the benefit of applying ultrasonic pretreatment in anaerobic digestion, it was compared with other pretreatment results obtained in other studies. For example, jingbo et al. used aerobic hydrolysis as a process that involves the breakdown of organic matter in the presence of oxygen. The treatment was used to improve the biodegradability of lignocellulose and enhance methane production performance. The results showed that after 16 h of aerobic hydrolysis methane production increased by 6 % from 252.59 to 268.75 (ml/g VS) [45]. Another study by Chebet et al. investigated the effects of thermochemical pre-treatment on biogas production from sweet potato root waste (SPW). According to the results of this study, the application of thermochemical pre-treatment using NaOH at a concentration of 2.9 g/L, a temperature of 82 °C, and a pre-treatment duration of 102 min resulted in a significant improvement in biogas and methane yields. Specifically, the pretreated SPW exhibited a 33.88 % increase in biogas yield and a 22 % increase in methane yield compared to the untreated SPW [46]. However, ultrasonic pretreatment has several advantages such as being relatively energy-efficient compared to other pretreatment methods such as thermal or chemical treatments. It requires lower energy input, making it a more sustainable option for biomass pretreatment. Unlike chemical pretreatment methods that rely on the use of harsh chemicals, ultrasound pretreatment is a chemical-free process. This eliminates the need for chemical reagents, minimizing the environmental impact and reducing the costs associated with chemical procurement and disposal. Lastly, ultrasound pretreatment can be easily scaled up for industrial applications. It can be integrated into existing anaerobic digestion systems without requiring significant modifications, making it a convenient and adaptable pretreatment option.

3.3. Model validation for optimum conditions

Finally, to ensure the veracity of the suggested model for maximum methane yield, a confirmation experiment was performed considering optimal conditions given by the model (actual pH: 8.11, the volume of Inoculum: 38 ml, and time of pretreatment: 45 min) for maximum bio-methane potential. Nevertheless, during the optimization process, several criteria were taken in consideration, not only the methane yield. Among these criteria are, the minimization of the feed pH by using the actual leachate pH, the minimization of the inoculum volume compared to the leachate volume, and the minimization of the pretreatment time.

At these optimum points, the results correspond to the predicted maximum bio-methane potential was 173 ml CH_4/g VS. The optimal conditions obtained were conducted in three experiments to validate the equations of the proposed model. The experimental results show that the bio-methane potential was 177 ml CH_4/g VS. It means that the obtained results were very close to the quadratic model's predictions (Table 5).

The present results suggest that RSM is a successful design approach for modelling and optimization of the bio-methane potential of anaerobic digestion.

The anaerobic digestion of the optimization test was monitored by FTIR (Fourier transform infrared) analysis. The FTIR spectra were used to study the possible change in chemical composition and functional groups of leachates after anaerobic digestion, confirming that some of the organic matter was transformed into CH_4. Table 6 shows all the vibrations before and after anaerobic digestion.

In Fig. 6, the broad absorption band at 3319 cm^{-1} is attributed to O–H vibrations of alcoholic and carboxylic groups [47]. The peak at 2955 cm^{-1} is attributed to aliphatic C–H [48]. The strong absorption at 2355 cm^{-1} is attributed to C–H aromatic. while the band at 1556 cm^{-1} and 1583 cm^{-1} can be attributed to aromatic structures or amides [49]. The absorption at 1413-1419 cm^{-1} has been attributed to aliphatic C–H deformation of structures such as fatty acids [50], and finally the band at 1033 and 1080 cm^{-1} is characteristic of carbohydrates and alcohol functions of polysaccharides [51].

As shown in Fig. 6 The majority of peaks were shifted, and the transmittance of some functional groups after anaerobic digestion decreased significantly, as for example in peaks 1033-1080 cm^{-1}, indicating the changes of functional groups in the leachate. This confirms the degradation of biodegradable organic matter present in the landfill leachate.

3.4. Digestate quality

The main objective of anaerobic digestion is to degrade the organic matter and produce a valuable gas which is methane, but we still have a residue which is the digestate. The landfill leachate digestate (LLD) has been dried and captured using the scanning electron microscope (SEM) coupled to an EDS analyzer sensor.

Fig. 7 shows the SEM of the solid landfill leachate digestate. In a wide range of particle sizes, a heterogeneous range of unevenly distributed structural features was observed with a non-smooth surface. Kameswari et al. indicated that the existence of irregular surface with cavities in the micrograph of the digestate is probably due to the transformation of particles into methane during methanization [52].

Table 5
Optimum conditions for anaerobic digestion of leachate.

pH	Inoculum (ml)	Pretreatment (min)	Bio-methane potential (ml CH4/g VS)	
			Predicted	Experimental
8.11	38	45	173	177

Table 6
Main absorbance bands observed by FTIR spectra in landfill leachate before and after anaerobic digestion.

Wavenumber (cm^{-1})	Vibration
400~885	Small sharp peaks, metal-alkyl stretching vibration
1033–1080	C–O stretching of polysaccharides
1413–1419	C–H stretching in aliphatic structures
1556–1583	Aromatic C=C, Amide (II)
2355	C–H aromatic
2960	C–H stretching of alkyl structures
3319	-OH (phenols, alcohols, and carboxylic groups)

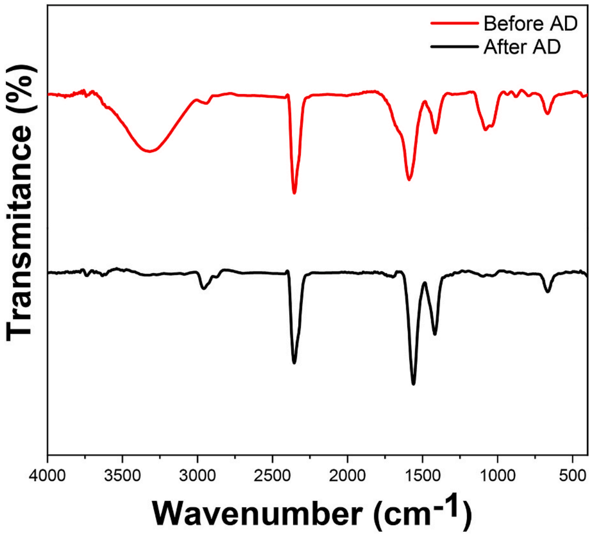


Fig. 6. FTIR spectra of landfill leachate before and after anaerobic digestion.

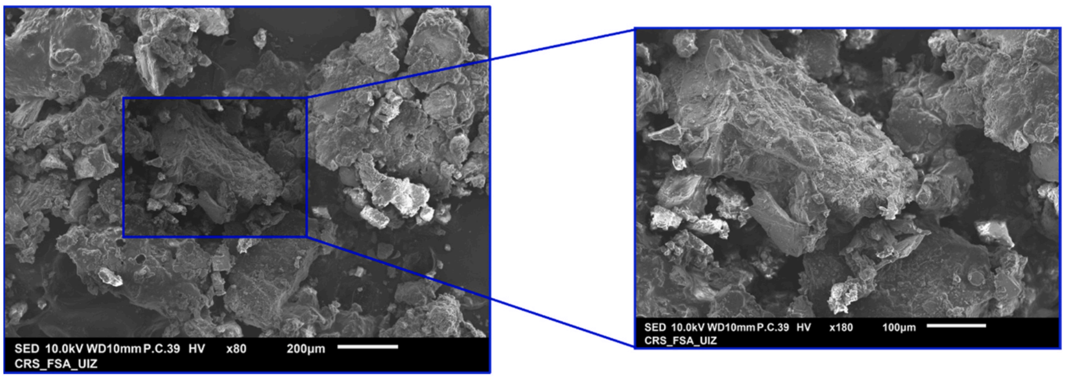
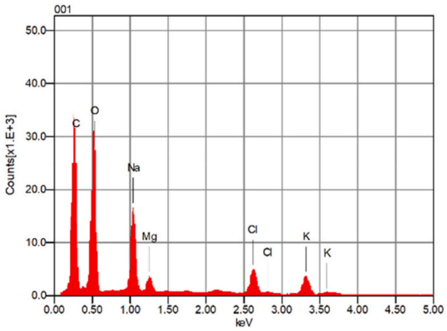


Fig. 7. Scanning Electron Micrograph of digestate.

The results of EDS (Fig. 8) showed that the proportion of these elements was relatively stable. The primary component was O (35.69 %), followed by C (31.37 %), Na (12.36 %), K (9.96 %), Cl (8.52 %), and Mg (2.10 %). The high levels of oxygen and carbon indicate that the digestate is rich in organic matter, which can be a valuable nutrient source for agricultural purposes or as a soil amendment [53]. In addition, the presence of potassium, sodium, and magnesium in the digestate suggests that it may have potential as a fertilizer for crop production. On the other hand, and in accordance with the morphology and characterization of LLD, pyrolysis is selected as the valorization and resource conversion ways of LLD. Biochar can be produced by pyrolyzing landfill leachate digestate. The highly porous reactive surface and structural characteristics of this material make it suitable for environmental depollution applications as well, For instance the removal of phenolic compounds, phenanthrene or dyes. A similar study conducted by Anfar et al. was used pyrolysis of Agri-food organic waste digestate as a recovery source to prepare a new low-cost adsorbent for methylene blue



Formula	Mass%	Atom%	Sigma	Net	K ratio	Line
C	31.37	43.81	0.01	399550	0.0652389	K
O	35.69	37.42	0.03	516690	0.3405780	K
Na	12.36	9.02	0.02	340356	0.2248223	K
Mg*	2.10	1.45	0.01	64735	0.0422602	K
Cl	8.52	4.03	0.03	144822	0.2120996	K
K	9.96	4.27	0.04	116634	0.2508071	K
Total	100.00	100.00				

Fig. 8. Elements present in the digestate determined using SEM-EDS.

removal, which the digestate characterized by Carbon (66.62 %), Oxygen (30.17 %), Calcium (0.53 %), Sodium (0.80 %), Phosphorus (0.50 %), Potassium (0.34 %), Aluminium (0.49 %), Chlorine (0.32 %), Tantalum (0.04 %), Gallium (0.18 %) [54]. Other studies have also treated the digestate from anaerobic digestion by pyrolysis for adsorption application [55–57]. Therefore, the EDS analysis allows us to make an approximate comparison with other works, which agree with our case.

4. Conclusion

In the present study, anaerobic digestion of landfill leachate was evaluated using CCD-RSM to model and optimize the operating parameter conditions required for methane production. The proposed model was statistically validated by analysis of variance (ANOVA) and was effectively used for estimation of methane production from anaerobic digestion of landfill leachate. The optimal conditions obtained after running the model reached a methane production of 177 ml CH_4/g VS. Considering these results, the integration of ultrasonic pre-treatment with anaerobic digestion for leachate treatment could lead to a higher yield and methane quantity.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Salaheddine Farsad: Conceptualization, Data curation, Formal analysis, Methodology, Writing – original draft. **Aboubakr Ben Hamou:** Data curation, Investigation, Methodology, Writing – review & editing. **Ayoub Chaoui:** Data curation, Investigation, Methodology, Writing – review & editing. **Asma Amjlef:** Data curation, Investigation, Writing – review & editing. **Saaida Lhanafi:** Investigation, Validation, Visualization. **Said Et-Taleb:** Investigation, Validation, Visualization. **Noureddine El Alem:** Project administration, Supervision, Validation, Visualization.

Declaration of competing interest

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

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