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Research Paper

The use of design of experiments for the evaluation of the production of surface rich activated carbon from sewage sludge via microwave and conventional pyrolysis

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HIGHLIGHTS

- Using of DOE for preparation of AC by conventional and microwave pyrolysis.
- The significant parameters in producing activated carbon were investigated.
- Conventional pyrolysis AC had better textural development than microwave AC.
- Temperature and holding time had significant influence on the S_{BET}.
- Reduction of production cost of activated carbon.

Keywords:
Sewage sludge
Statistical design of experiments
Microwave and conventional pyrolysis
Activated carbon

ABSTRACT

Experimental design and response surface methodology were used for the preparation and comparison of activated carbon produced from sewage sludge by two types of pyrolysis: conventional furnace and microwave. The preparation method was performed following a full fractional factorial design (2^3), including pyrolysis temperature or power radiation, holding time and chemical activation agent, and specific surface area (S_{BET}) of prepared activated carbon. The influence of these factors on the S_{BET} of obtained carbon was investigated using an analysis of variance. Samples made by conventional pyrolysis showed overall higher S_{BET} values than samples synthesised by the microwave method. The optimum parameters for the preparation of activated carbon using the conventional pyrolysis have been identified as: pyrolysis temperature of 500 °C, holding time of 15 min, and a ratio of $ZnCl_2$:sludge of 0.5. Microwave pyrolysis is found to be optimal when operating at 980 W for 12 min. Under these conditions, S_{BET} values of 679 and 501 m^2g^{-1}, respectively, have been obtained. The analysis of nitrogen adsorption/desorption isotherms revealed the presence of micro and mesopores in the activated carbon. The most important significant factor, according statistical analysis, in the variance in S_{BET} for the conventional pyrolysis samples were the pyrolysis temperature and interaction between pyrolysis temperature, holding time and ratio of $ZnCl_2$:sludge were the most important factors. The highest impact parameters for the microwave method were found for the interaction between power radiation and ratio of $ZnCl_2$:sludge and the holding time.

1. Introduction

The growing urbanisation of global society, coupled with increasingly stringent sludge reuse/disposal regulations and increasing public pressure, is forcing both public and private sludge generators to evaluate their sludge management strategies [1,2]. Conventionally, waste sludge is disposed of via incineration, landfilling, and as soil conditioner in agriculture. However, in recent years, new applications for sewage sludge, such as production of ceramic materials [3,4] and activated carbon [5–7] have been explored.

Activated carbon is generally produced from natural starting materials (e.g. coconut shells) by pyrolysis under inert atmosphere at

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elevated temperatures. The temperature treatment can be conducted by conventional heating in a furnace, or by microwave-assisted pyrolysis. The main difference between conventional pyrolysis and the microwave-assisted method is the way the heat is generated. Microwaves supply energy directly to the carbon bed [8,9]. Energy transfer is not by conduction or convection as in conventional heating, but microwave energy is readily transformed into heat inside the particles by dipole rotation and ionic conduction [8,9]. Thus, it has the advantages of rapid temperature rise, uniform temperature distribution, and energy savings over conventional thermal methods [8,10]. However, current literature is not clear about which method produces adsorbents with higher specific surface areas (S_{BET}). Different work comes to different conclusions about different starting materials; for instance, with oil palm shell as the starting material, conventional pyrolysis obtains higher S_{BET} than microwave [11]. Conversely, activated carbon prepared from olive pits obtained higher S_{BET} with the microwave-assisted heating process [12,13].

The properties, especially S_{BET}, of activated carbon depend on variables like feedstock type and source, pyrolysis temperature, radiation power, and holding time [13,14]. Because of these very controllable parameters, pyrolytic methods are highly versatile processes where it is possible to optimise these variables to get activated carbon with higher S_{BET} [13,14].

The properties of activated carbon such as S_{BET} can be improved using experimental design by response surface methodology (RSM). RSM is a very valuable tool for this purpose as it presents statistical models which can be used to understand the interactions between the parameters that have been optimised [15–17]. RSM has been applied widely in various processes for the optimisation of experimental conditions, and should prove useful for the preparation of activated carbon. As reported recently, RSM was applied in the production of AC using different precursors such as Turkish lignite [17], Albizia lebbeck seed pods [18], Bamboo [19], Jatropha Hull [20], polycarbonate [21] and coconut shell [22].

To this point, it does not appear that RSM has been applied to study the comparison of the preparation of activated carbon from sludge sewage by conventional pyrolysis versus microwave-assisted pyrolysis.

This work aims to apply RSM to evaluate how microwave and conventional pyrolysis methods, and the pyrolysis conditions: pyrolysis temperature/applied microwave power, holding time, and ratios of chemical agents, can be optimised for maximum effect on the S_{BET} of activated carbon from sewage sludge.

2. Materials and methods

2.1. Experimental design

In this work, a 2^3 full factorial design with 3 central points was studied. The factors used for the production of activated carbon from sewage sludge were studied with standard RSM in order to identify and optimise the effective process parameters. In addition, this method helps to analyse the interaction between these parameters [15,16]. With this method, a core factorial is created that forms a cube with sides that are two coded units in length (from –1 to +1); noted in the Table 1. Table 1 shows the ranges and the levels of the variables examined and their combinations in this study. The studied variables were: activation temperature or microwave power ($X1$), chemical impregnation ratio ($X2$), and holding time ($X3$). In order to minimise the effects of the uncontrolled factors, the experimental sequence was randomised, as can be seen in Table 1. It shows the number of runs and their respective parameter combinations to activated carbon samples made by conventional pyrolysis and microwave. It was assumed that the relationship between the three independent variables and the experimental S_{BET} data follow a linear equation, as expressed in Eq. (1):

$$R = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1 X_2 + \beta_5 X_1 X_3 + \beta_6 X_2 X_3 + \beta_7 X_1 X_2 X_3 + \varepsilon \quad (1)$$

Where R is the predicted response; X_1 to X_3, coded variables; β_o, the constant coefficient; β_1 to β_3, the linear term coefficients; β_4 to β_6, the interaction coefficients between two variables and β_7, the interaction coefficients between three variables.

2.2. Preparation of sludge-derived activated carbon

The raw material used for preparing the activated carbon was sewage sludge obtained from a municipal wastewater treatment plant in Porto Alegre, Brazil. First, the sludge was dried at 105 °C for 24 h until no further weight loss could be detected. Subsequently, it was crushed with a grinder, and sieved to a size range

Table 1
Design of experiments for preparation of activated carbon by conventional and microwave pyrolysis.

Factor	Name	Conventional			Microwave		
		Variable level					
		–1	0	+1	–1	0	+1
		–1	0	+1	–1	0	+1
X1	Temperature and power	500	650	800	700	840	980
X2	Hold time	15	37.5	60	8	10	12
X3	Ratio: $ZnCl_2$/sludge	0.5	1.0	1.5	0.5	1.0	1.5

Experiments samples	Coded variables			Conventional			Microwave		
	T_f	t_r	m	T_f	t_r	m	Pow	t_r	m
500-15-0.5 and 700-8-0.5	–1	–1	–1	500	15	0.5	700	8	0.5
800-15-0.5 and 980-8-0.5	+1	–1	–1	800	15	0.5	980	8	0.5
500-60-0.5 and 700-12-0.5	–1	+1	–1	500	60	0.5	700	12	0.5
800-60-0.5 and 980-12-0.5	+1	+1	–1	800	60	0.5	980	12	0.5
500-15-1.5 and 700-8-1.5	–1	–1	+1	500	15	1.5	700	8	1.5
800-15-1.5 and 980-8-1.5	+1	–1	+1	800	15	1.5	980	8	1.5
500-60-1.5 and 700-12-1.5	–1	+1	+1	500	60	1.5	700	12	1.5
800-60-1.5 and 980-12-1.5	+1	+1	+1	800	60	1.5	980	12	1.5
650-37-1.0 and 840-10-1.0	0	0	0	650	37.5	1.0	840	10	1.0
650-37-1.0 and 840-10-1.0	0	0	0	650	37.5	1.0	840	10	1.0
650-37-1.0 and 840-10-1.0	0	0	0	650	37.5	1.0	840	10	1.0

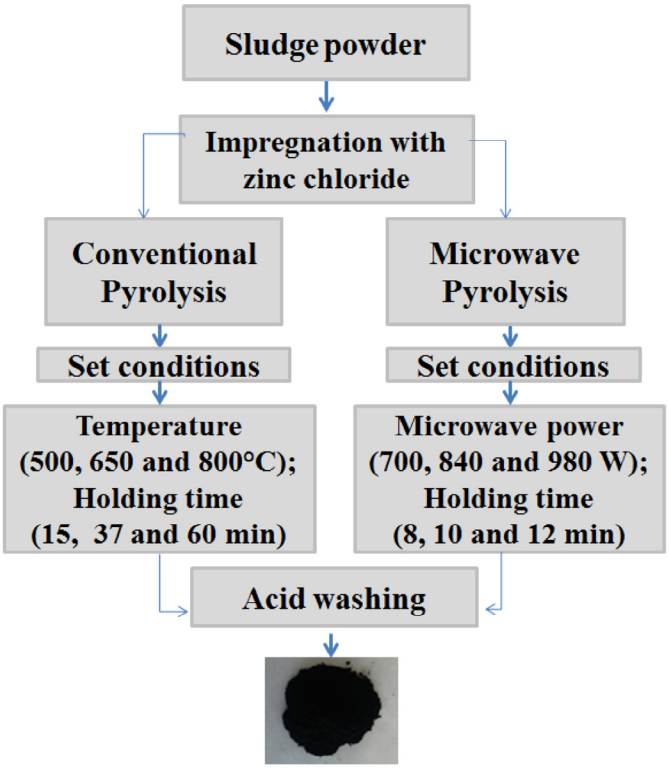


Fig. 1. Scheme of preparation steps of the activated carbon made by conventional and microwave pyrolysis and varied parameters.

below 250 µm. An overview of preparation of activated carbon is showed in the Fig. 1.

The preparation of the sludge-based activated carbon was comprised of three main steps:

(a) 10.0 g of dried, powdered sewage sludge was mixed with $ZnCl_2$ at various $ZnCl_2$:sludge ratios (see Table 1). Afterwards, 5.0 mL of water was added, and thoroughly mixed to obtain a homogeneous paste. The paste was placed in a crucible and dried at room temperature for 24 h.
(b) Temperature and activation time of pyrolysis for each sample is listed in Table 1. Pyrolysis processes were performed under a steady-state flow of nitrogen (inert) gas with a flow rate of 100 mL/min, and at a constant heating rate of 5 °C/min (conventional furnace) or set to a constant power output (microwave-assisted pyrolysis, see Table 1).
(c) To complete the chemical activation by leaching the remaining $ZnCl_2$ out of the pyrolysed carbon, and in order to enhance the specific area of the AC, the samples were washed with 6.0 mol L^{-1} HCl [23]. For this, 8.0 g of AC was added to 150 mL of 6 mol L^{-1} HCl in a 250 mL flask; the mixture was stirred on a magnetic stirrer under reflux for 3 h at 75 °C. Subsequently, the slurry was cooled down and vacuum filtered through 0.45 µm polycarbonate membranes. After extensive washing with distilled water, the solid material was oven dried at 105 °C for 5 hours, and hand milled to a particle size ≤ 150 µm.

2.3. Sample nomenclature

The pyrolysed materials investigated in this study are listed in Table 1. The first number in the sample name refers to the temperature or the power used in the pyrolysis, followed by the holding time, and ratio of $ZnCl_2$:sludge. For example, "500-15-0.5" was prepared using conventional pyrolysis at 500 °C, with 15 minutes of holding time, and a weight ratio of 0.5:1.0 of $ZnCl_2$:sludge. "980-12-1.5" was prepared with microwave pyrolysis at 980 W of power, with 12 minutes of holding time, and a weight ratio of 1.5:1.0 of $ZnCl_2$:sludge.

An overview of the conditions under which the samples of sewage sludge were pyrolysed is presented in Table 1.

Where "T" is the pyrolysis temperature (°C), "P" is the power radiation, "t" is the holding time and "Ratio" is the ratio of$ZnCl_2$:sludge.

The specific surface area (S_{BET}) was the parameter chosen as a "response", in order to characterise the activated carbon product.

2.4. Characterisation of the activated carbon

For nitrogen adsorption/desorption experiments, the AC was crushed into a fine powder (<250 µm) for analysis in order to diminish diffusion limitations that can occur for larger particles. Nitrogen adsorption isotherms were recorded with a commercial system (Belsorp-Mini, Bel Japan Inc.) at 77 K after drying for 3 h at 393 K under reduced pressure (<2 mbar). The S_{BET} were determined using the method of Brunauer, Emmett, and Teller (BET) [24]. The pore size distributions were calculated from the desorption branch of the isotherms based on the Barrett–Joyner–Halenda (BJH) model [25].

Elemental (C, H, N) analyses of samples were performed on a CHNOS Elemental Analyser (Elementar, Vario EL III, Germany). The yields of ash in sludge and AC were analysed by burning them in a muffle furnace at 600 °C for 30 min [26,27].

3. Results and discussion

3.1. Elemental analysis of sewage sludge and activated carbon

An elemental analysis was used to determine the carbon, hydrogen, and nitrogen composition of the sample. Oxygen composition was determined by subtracting the sum of the percentages of carbon, hydrogen, nitrogen, and ashes from the 100% total [11,26,27]. Elemental analyses and ash contents of raw sewage sludge and the activated carbon prepared with the lowest and highest surface areas by the microwave (980-8-1.5 and 980-12-0.5) and conventional method (800-15-1.5 and 500-15-0.5) are shown in Table 2.

The CHN analysis clearly shows little difference in the carbon content on the adsorbents made from conventional or microwave-assisted pyrolysis. This suggests that both types of pyrolysis work well for activated carbon production.

Although similar for all samples, relative C content was slightly reduced at higher [conventional] pyrolysis temperatures and increased holding times (microwave-assisted).

Table 2
Element analysis of sewage sludge and activated carbon with lowest and highest specific surface area of both kind of pyrolysis.

	Ash[a]	Elemental composition[b] (%)			
		C	H	N	O[c]
Sewage sludge	46.24	32.68	5.12	6.17	9.79
Conventional heating					
500-15-0.5	52.36	36.40	1.73	3.24	6.27
800-15-1.5	61.09	31.32	1.07	1.56	4.96
Microwave-assisted					
980-12-0.5	57.85	32.02	2.10	2.70	5.33
980-8-1.5	51.73	34.46	2.57	3.99	7.25

[a] On dry basis.
[b] On dry and ash free basis.
[c] By difference, O = 100% – (C + H + N + Ash).

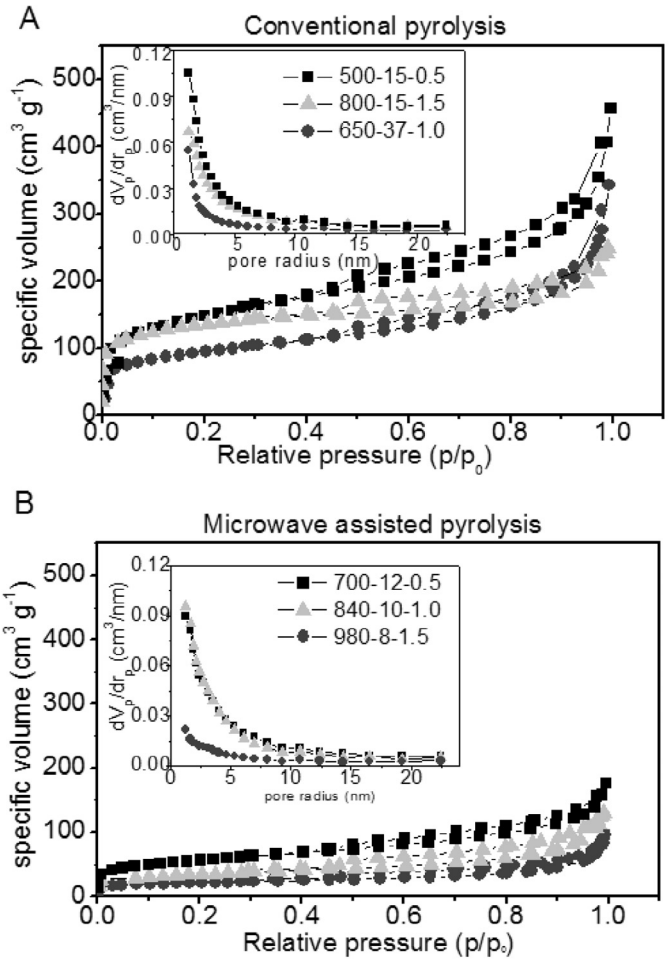


Fig. 2. Nitrogen adsorption/desorption isotherms for activated carbon made by conventional (A) and microwave (B) pyrolysis and their corresponding BJH plots.

Additionally, it can be shown that a decrease in hydrogen contents occurs (from sewage sludge at 5.12% to 1.07–1.73% and 2.10–2.57% for conventional and microwave pyrolysis, respectively), due to the rupturing of molecular chains at high temperatures [27]. Nitrogen and oxygen content displayed a similar trend, with the sludge losing nitrogen and oxygen during pyrolysis. As expected, microwave and conventional pyrolysis favours the elimination of nitrogenous and hydrogen compounds as volatile gases [26]. The loss of oxygen content (in addition to other volatiles) suggest that a large number of functional groups were lost during pyrolysis [11].

3.2. Porosity – comparisons between conventional and microwave method

The comparison of microwave and conventional pyrolysis was performed in order to determine which method produces activated carbon with higher S_{BET}, which were determined for all samples by nitrogen adsorption–desorption isotherms. Fig. 2A and B show the isotherms of three selected samples from each pyrolysis method (other samples show similar isotherms).

All pyrolysed samples can be assigned a type IV isotherm according to International Union of Pure and Applied Chemistry (IUPAC) classification. Type IV isotherms possess a hysteresis loop, representing capillary condensation, indicating the presence of mesopores [28–30]. However, it should be noted that the adsorbed N_2 volumes are different, depending on the pyrolysis method applied (Fig. 2A and B). The range of nitrogen volumes adsorbed by activated carbon produced by conventional pyrolysis was slightly more than double (227–458 $cm^3\ g^{-1}$) those produced by microwave (91–187 $cm^3\ g^{-1}$).

According to the standard adsorption classification of IUPAC, micropores have diameters lower than 2 nm, mesopores have diameters between 2 and 50 nm, and macropores' are higher than 50 nm. All samples produced by both pyrolysis processes have micropores and mesopores, as illustrated in the BJH plots (Fig. 2A and B).

Structural heterogeneity and solid internal structure can be represented by characterisation of the pore size distribution [15]. The pore size distributions derived from the BJH plots of the conventional and microwave samples are shown in Fig. 2A and B, respectively. The pyrolysis conditions of each method appear to affect the pore structure of the activated carbon, in addition to the method used (see Fig. 2A and B). By increasing the temperature, the samples pyrolysed by conventional means showed a sharp peak in the range of large micropores or small mesopores. Activated carbon produced at higher temperatures, according to the BJH plots, possessed homogeneous, small mesopores.

The creation of large micropores and small mesopores, increased with the sample 500-15-0.5, which is in good agreement with the increase in adsorbed specific volume of N_2 according to the isotherm of nitrogen (see Fig. 2A) for the conventional method. The microwave activated carbons also demonstrated a relatively broad peak in the micropore and mesopore range (see Fig. 2B). However, the AC samples obtained via microwave heating show S_{BET} and specific volume of pores rather smaller than the AC obtained via conventional pyrolysis. The microwave radiation has a strong influence on AC structure. AC processed by microwave heating has a different pore structure; a smaller surface area allocated to micropores, and a higher bulk density than the conventional method [31]. This difference might be the result of radiation action on the decomposition kinetics of the organic compounds, leading to a more condensed/dense network [31] that decreases the S_{BET} in comparison to AC produced by conventional pyrolysis. However, it should be noted that the samples produced via both methods show approximately the same textural properties. This implies that the quick, volumetric heating provided by the microwave technique promotes the development of pores in a shorter amount of time than conventional pyrolysis, which saves energy.

Fig. 3 shows the S_{BET} of all activated carbon samples, and it can be seen that the S_{BET} derived from conventional pyrolysis were higher than the S_{BET} of AC made by microwave-assisted pyrolysis over the whole set of conditions. The highest S_{BET} was found for a sample made by conventional method (679 $m^2\ g^{-1}$), which is about 35.52% higher than the highest S_{BET} of a sample made by microwave pyrolysis (501 $m^2\ g^{-1}$). These results show that, under these experimental conditions, conventional pyrolysis was more efficient at generating high S_{BET} values than the microwave-assisted pyrolysis. It remains possible that the differences may have arisen if the holding time was not high enough to promote the total carbonisation of the samples. However, not all samples pyrolysed for 12 min show high S_{BET}.

A microwave activation time shorter than that employed for conventional activation was chosen for the following reasons: in light of a previous study on sludge where the materials exhibited the highest ash content at an activation time of 15 min (at conditions established in this study), and consequently lower S_{BET}. Although, in the literature the activation times for the microwave pyrolysis differ from 30 s to 30 min, the precursors can influence the decomposition behaviour such that each precursor has its own optimal activation time [32–35].

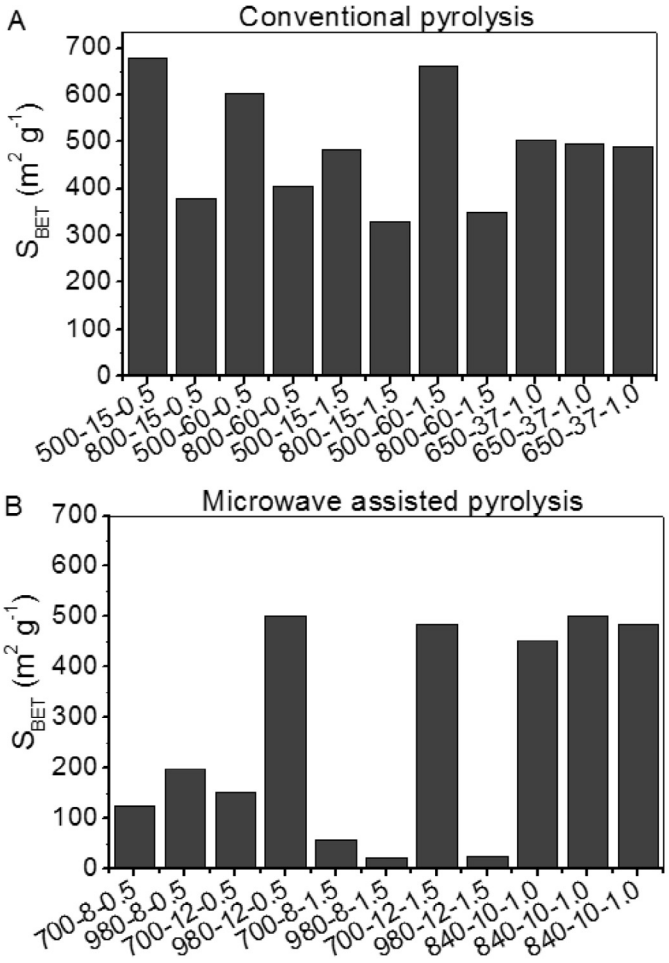


Fig. 3. Specific surface areas of activated carbon made by conventional (A) and microwave assisted pyrolysis (B).

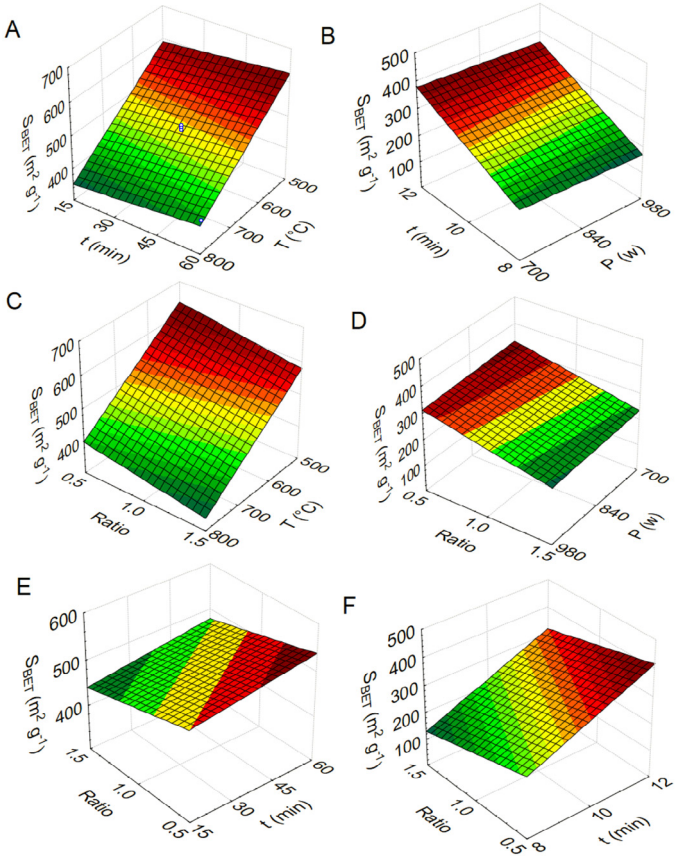


Fig. 4. (A) 3D response surface: Interactive effects of varied holding time and pyrolysis temperature (°C) on response S_{BET}. (B) 3D response surface: Interactive effects of varied ratio of $ZnCl_2$:sludge and pyrolysis temperature on response S_{BET}. (C) 3D response surface: Interactive effects of varied ratio of $ZnCl_2$:sludge and holding time (minutes) on response S_{BET}. (D) 3D response surface: Interactive effects of varied holding time and power radiation on response S_{BET}. (E) 3D response surface: Interactive effects of varied ratio of $ZnCl_2$:sludge and power radiation on response S_{BET}. (F) 3D response surface: Interactive effects of varied ratio of $ZnCl_2$:sludge and holding time on response S_{BET}.

3.3. *Analysis of the response surface plots and statistical analysis*

The results of the S_{BET} from the activated carbon pyrolysed by conventional pyrolysis and microwave assisted were analysed with an ANOVA for a 2^3 factorial design and also for the response surface plots.

Fig. 4 shows the effect of the variables on the response (S_{BET}) using 3D response surface graphs, obtained by combination of the various pyrolysis parameters (Table 1) and the resulting S_{BET} values (Fig. 4A–F).

Concerning activated carbon made by conventional pyrolysis, Fig. 4A shows interactions between holding time and pyrolysis temperature, and it is observed that the highest S_{BET} values are located in the region defined by lower pyrolysis temperatures. For activated carbon samples derived from microwave pyrolysis, the best S_{BET} results were obtained with a higher holding time (see Fig. 4B). Fig. 4C demonstrates the interactions between the ratio of $ZnCl_2$:sludge and the pyrolysis temperature; S_{BET} values increase while both parameters drop. On the other hand, samples produced with microwave-assisted pyrolysis showed that S_{BET} values were largely unaffected by both parameters (see Fig. 4D).

Fig. 4 illustrates the behaviour of the studied variables on the S_{BET} response; however, it is not possible to understand which variables were more important in terms of their interactions and how each one influenced the S_{BET} response. For this purpose, Pareto Charts have been showed and analysed. Fig. 5A and B presents the Pareto Charts for standardised effects at p = 0.05, for activated carbon made by conventional and microwave pyrolysis, respectively. In addition, normal probability plots of standardised effects at p = 0.05, for activated carbon made by conventional and microwave pyrolysis, respectively, are shown in Fig. 5C and D. The bars visualise the variables (*X1-X3*) and their interactions (e.g. *X1X2X3*). In this diagram, all bars that are located to the right of the vertical dashed line are significant, which means that the variables and/or their interactions influenced the S_{BET} response at a minimum statistically significant level of 95% confidence.

The results presented in Fig. 5A and B and Table 3 indicate that for activated carbon made by conventional pyrolysis, the most important factors influencing the S_{BET} values were (in descending order): pyrolysis temperature (X1), the interaction between pyrolysis temperature with holding time and ratio of $ZnCl_2$:sludge (X1X2X3), followed by holding time and ratio of $ZnCl_2$:sludge (X2X3), ratio of $ZnCl_2$:sludge (X3) and holding time (X2). The most important factors influencing the S_{BET} values for microwave pyrolysis samples were, in descending order: interactions between power and ratio of $ZnCl_2$:sludge (X1X3), holding time (X2), interactions between power radiation, holding time and ratio of $ZnCl_2$:sludge (X1X2X3), and the ratio of $ZnCl_2$:sludge (X3).

The Pareto chart assists in ascertaining which of the factors and its interactions are most important [36]. However, to complement this analysis, it is important to plot the normal probability of

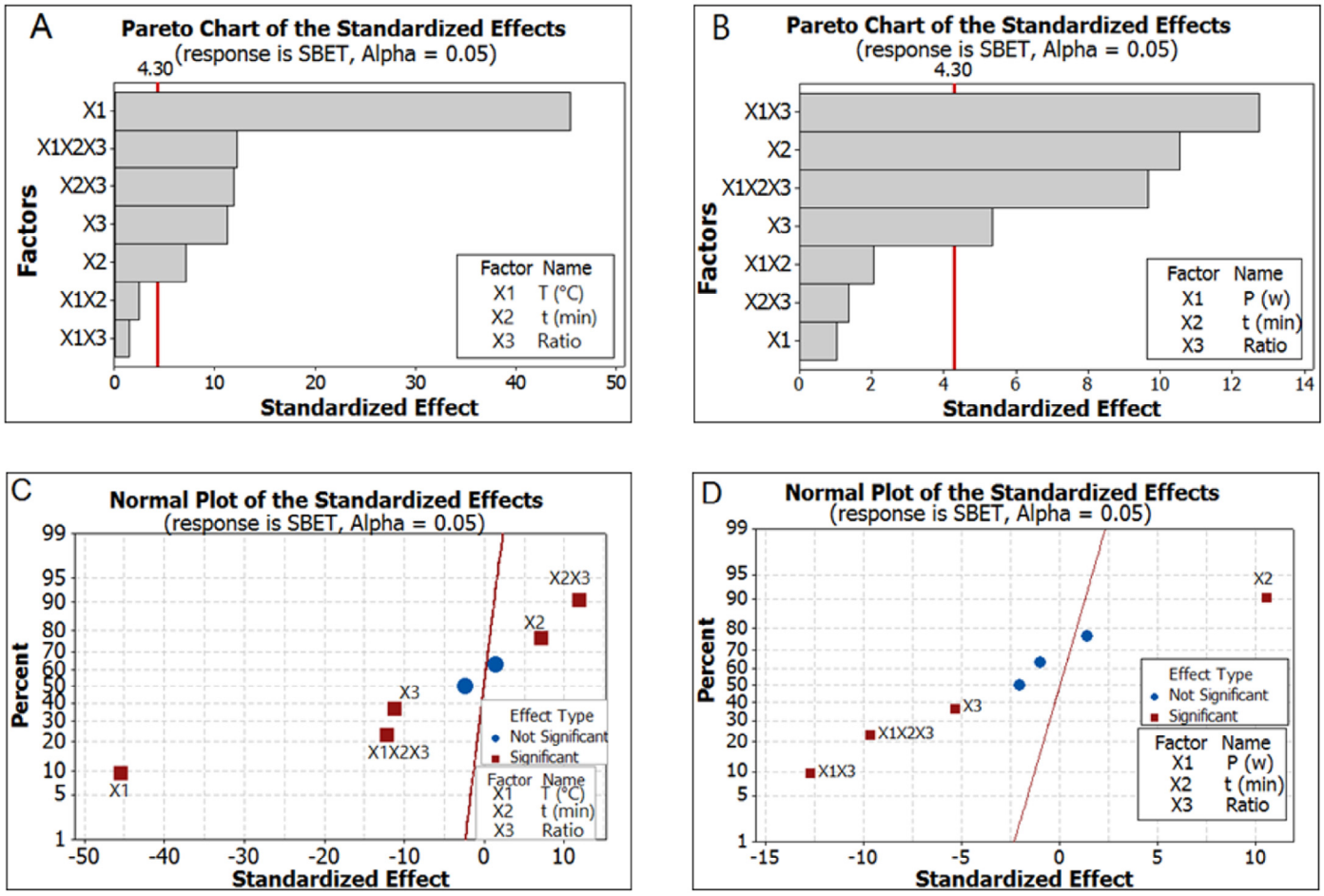


Fig. 5. (A,B) Pareto plots of standardised effects at p = 0.05, for activated carbon made by conventional and microwave pyrolysis, respectively. (C,D) Normal plots of standardised effects at p = 0.05, for activated carbon made by conventional and microwave pyrolysis, respectively. The dotted line at 50% divides the negative effects from the positive ones.

standardised effects at p = 0.05 for activated carbon made by conventional and microwave pyrolysis (Fig. 5C and D). The fit line indicates the values expected to be obtained when the parameters would have no effect. Significant effects are shown with their labels and situated a certain distance to the left or right of the fit line showing negative (when the points are situated left to fit line) or positive values (when the points are situated right to fit line) of the standardised effect. Positive values for effects mean that an increase in their levels lead to an increase in the S_{BET} of the activated carbon; negative values lower the S_{BET} with increasing level.

Table 3
Estimated effects and coefficients for S_{BET} at 95% of probability.

Term	Kind of pyrolysis					
	Conventional pyrolysis			Microwave assisted		
	Effect	Coeff	SE Coeff	Effect	Coeff	SE Coeff
Constant		486.1	2.654		195.4	9.028
X1	−241.2	−120.6	2.654	−18.7	−9.4	9.028
X2	37.7	18.9	2.654	190.2	95.1	9.028
X3	−59.8	−29.9	2.654	−96.8	−48.4	9.028
X1X2	−12.8	−6.4	2.654	−37.2	−18.6	9.028
X1X3	7.7	3.9	2.654	−230.3	−115.1	9.028
X2X3	62.7	31.4	2.654	24.8	12.4	9.028
X1X2X3	−64.8	−32.4	2.654	−174.7	−87.4	9.028

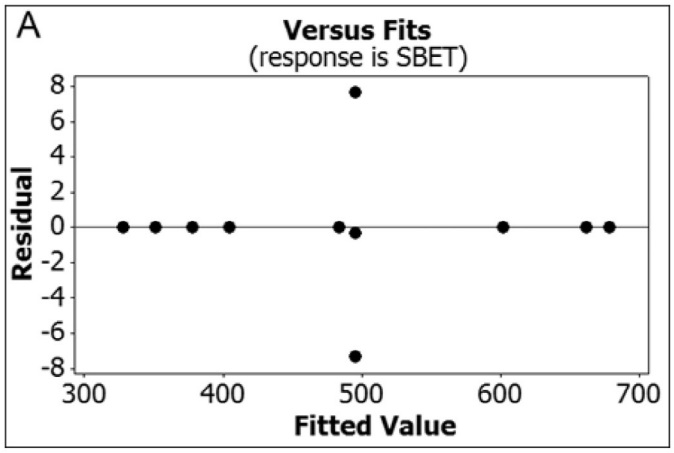
Note: Microwave assisted pyrolysis – $R^2_{Adj} = 0.9857$; Conventional pyrolysis – $R^2_{Adj} = 0.9961$.

Variables having a negative effect were X1, X3, and X1X2X3 for samples derived from conventional pyrolysis, and X1X3, X1X2X3, and X3 for samples made using the microwave method. The variables with positive effects on the activated carbon synthesis were X2X3 (conventional method), and X2 (conventional and microwave). The optimal conditions for S_{BET} of activated carbon were extracted by comparing the observed values with the values predicted by the model. Fig. 6A and B presents the residuals versus fit values for the production of activated carbon by conventional and microwave pyrolysis, respectively. This figure shows how closely the set of observed values follows a theoretical distribution. Generally, in both cases, experimental points are reasonably aligned suggesting a normal distribution. This suggests that the model used in the statistical analysis was appropriate, and can be used to predict the set of conditions leading to the best results (response S_{BET}).

3.4. Analysis of variance (ANOVA)

A systematic study using RSM has been carried out to justify the adequacy of the model used in the analysis of pyrolysis process variables. Table 3 shows the results of fitting Eq. (1) to the experimental data by linear regression analysis, and those obtained from evaluating the fitness of the model by means of ANOVA together with the adjusted determination coefficient (R^2_{Adj}).

The ANOVA tests show that the models for S_{BET} were statistically significant at a 95% confidence level ($p \leq 0.05$); their lack-of-fit



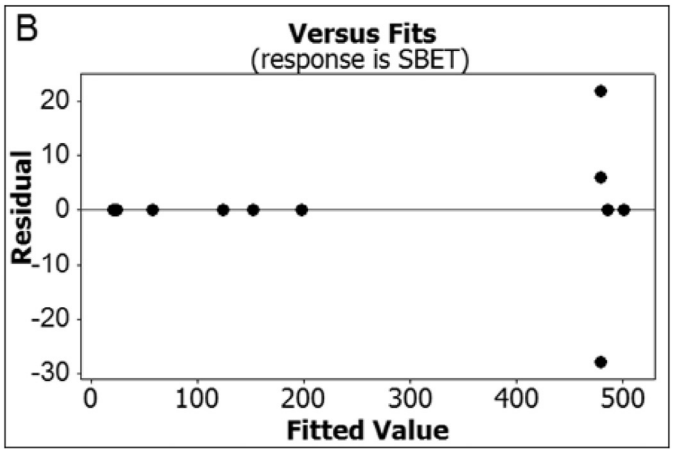


Fig. 6. Residuals versus fit values plot from activated carbon synthesised by conventional pyrolysis (A) and by microwave pyrolysis (B).

was found not to be statistically significant at a 95% confidence level ($p > 0.05$) (see Table 3). For regression analysis, the model was simplified (reduced by rejection of non-significant factors X1X2 and X1X3 for conventional pyrolysis and X1, X1X2, and X2X3 for microwave assisted pyrolysis) and the best fit model equations which describe the S_{BET} values of the activated carbon made by conventional and microwave pyrolysis are given by Eqs. (2)–(5), respectively:

$$S_{BET\ (Conventional)} = A_o + A_1X1 + A_2X2 + A_3X3 + A_6X2X3 + A_7X1X2X3 \quad (2)$$

$$S_{BET\ (Conventional)} = 486.1 - 120.6T + 18.9t - 29.9Ratio + 31.4t.Ratio - 32.4TtRatio \quad (3)$$

$$S_{BET\ (microwave)} = A_o + A_2X2 + A_3X3 + A_5X1X3 + A_7X1X2X3 \quad (4)$$

$$S_{BET\ (microwave)} = 195.4 + 95.1t - 48.4ratio - 115.1PRatio - 87.4PtRatio \quad (5)$$

The quality of the fit of the model was checked by the R^2_{Adj} between the experimental and model-predicted values of the response variable (Fig. 6A and B). To strengthen the arguments for the quality of our statistical analysis, Table 4 summarises the sum of squares used to estimate the factors effect and the F-ratios (defined as the ratio of the respective mean-square-effect and the mean-square-error). Furthermore, because the factors in this study have two levels, each ANOVA main effect and interaction effects have one degree of freedom [37].

Table 4
Analysis of Variance for S_{BET} from microwave and conventional pyrolysis.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Microwave assisted						
Main effects	3	91814	91814	30605	46.94	0.021
2-Way interactions	3	110030	110030	36677	56.25	0.018
3-Way interactions	1	61075	61075	61075	93.67	0.011
Curvature	1				269.19	0.004
Residual error	2	1304	1304	652		
Pure error	2	1304	1304	652		
Total	10	439736				
Conventional pyrolysis						
Main effects	3	126393	126393	42131	747.89	0.001
2-Way interactions	3	8320	8320	2773	49.23	0.020
3-Way interactions	1	8385	8385	8385	148.85	0.007
Curvature	1	185	185	185	3.28	0.212
Residual error	2	113	113	56		
Pure error	2	113	113	56		
Total	10					

Note: Microwave assisted pyrolysis – $R^2_{Adj} = 0.9857$; Conventional pyrolysis – $R^2_{Adj} = 0.9961$.

Whereby the p value is defined as the lowest level of significance leading to rejection of the null hypothesis, it would appear that the main effect of each factor and the interaction effects are statistically significant at $p < 0.05$ [36,37]. The results further strengthen the statistical significant of the studied factors and their interaction. Additionally, the values of $R^2_{Adj} = 98.57\%$ for microwave method and $R^2_{Adj} = 99.61\%$ for conventional method confirm the accuracy of the model.

4. Conclusions

In order to achieve the best conditions for the production of activated carbon with high surface area from sewage sludge, a full 2^3 factorial design was employed for screening the factors that would influence the overall optimisation of the pyrolysis procedure by microwave and conventional methods. The activated carbon produced had a mixture of micro- and mesopores.

The optimum conditions for preparation of activated carbon by the microwave method was of 980 W power, a holding time of 12 min, and ratio of $ZnCl_2$:sludge of 0.5. Under these conditions, an S_{BET} of 501 $m^2\ g^{-1}$ was obtained. Optimum conditions for conventional furnace pyrolysis were a pyrolysis temperature of 500 °C, a holding time of 15 min, and ratio of $ZnCl_2$:sludge of 0.5. Under these conditions, a S_{BET} of 679 $m^2\ g^{-1}$ was achieved.

The factor that most strongly influenced the S_{BET} values was the temperature (X1, negatively) for conventional furnace heating. On the other hand, for microwave assisted pyrolysis the holding time (X2) was the most important positive factor, followed by the interaction between temperature and ratio of $ZnCl_2$:sludge (X1X3, negative) in the response.

The data obtained for the two methods using sewage sludge as a starting material showed that conventional pyrolysis is preferable to the AC produced by microwave-assisted pyrolysis because activated carbon with higher specific areas were generated, and the accuracy of the model was slightly higher, according to R^2_{Adj}, with values of 0.9961 and 0.9857 for conventional and for microwave methods, respectively.

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