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SUSTAINABLE INDUSTRIAL AND ENVIRONMENTAL BIOPROCESSES

Study of biological and thermo-chemical pretreatment of organic fraction of municipal solid waste for enhanced biogas yield

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Abstract
Biogas production from organic fraction of municipal solid waste (OFMSW) not only helps in solid waste management but also combat the food vs fuel dilemma. The presence of lignocellulosic material and other complex compounds in OFMSW hinder biogas production. Therefore, pretreatment is an essential step to increase the hydrolysis rate by converting complex compounds to simpler ones. This work was aimed at effective pretreatment of OFMSW by biological and thermo-chemical means. For biological pretreatment lignin degrading fungal strains, *Phanerochaete chrysosporium* and *Pleurotus ostreatus* were employed. Thermo-chemical treatment resulted in higher solubilisation yield in terms of sCOD and VFA making it a more effective method as compared with biological pretreatment. The optimisation of thermo-chemical pretreatment was done by the Box-Behnken design of response surface methodology (RSM). The interactive effect of influencing factors NaOH dose, temperature and time were studied on the response of sCOD, VFA and phenolic content. The sCOD and VFA values were significantly increased by increasing the NaOH concentration, temperature and time to a certain limit. The optimised condition from RSM for maximum solubilisation yield in terms of sCOD, VFA and phenolic content was found to be NaOH dose of 4.72 g/L, temperature 180 °C and time 30.3 min. Biogas production was increased by 169.5% after pretreatment at RSM optimised conditions as compared with untreated OFMSW.

Keywords Municipal solid waste · Volatile fatty acid · Soluble chemical oxygen demand · Box-Behnken design · Response surface methodology

Introduction

The sustainable management of municipal solid waste (MSW) considers three components, environment, economic and social (Fernández-Braña et al. 2019). The various technologies, such as open burning, incineration, open dumping, landfilling and composting, are used for MSW disposal and management. MSW disposal through incineration results in the emission of toxic air pollutants, fly ash and fine particulates of bottom ash residue (Phua et al. 2019). The main problems associated with landfills are land availability, penetration of leachate to underground water, the outflow of methane to the atmosphere and need for leachate treatment (Escamilla-Alvarado et al. 2017). Various researches have been done on minimisation of adverse effects of different disposal methods and also finding out the best among them. In a case study, Yadav and Samaddar (2018) found out the recycling, composting and landfilling without energy recovery as the best method for MSW disposal. The biodegradable part of MSW generally adopts for composting or anaerobic digestion. The research is gaining focus on the management of OFMSW through anaerobic digestion (AD) as it provides potential alternative energy and promising waste disposal. AD is the series of steps that include hydrolysis, acidogenesis, acetogenesis and methanogenesis carried out by different microorganisms in anaerobic environment to produce biogas, a mixture of CH_4 (45–70%), CO_2 (24–40%) and some traces of N_2, H_2, H_2S, water vapour and halogenated hydrocarbons (Khan et al. 2017). Biogas production through AD process requires an optimum range of temperature (30–37 °C for mesophilic and 50–60 °C for thermophilic), pH (6.8–7.2), C/N ratio (15–30) and better biodegradability of the substrate

The original version of this article was revised: The original publication of this paper contains an error. The correct image for Fig. 1 is shown in this paper.

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(Zhang et al. 2014). Hydrolysis and methanogenesis are considered as the rate-determining steps in the AD process.

Although OFMSW is the organic biodegradable portion of MSW, it is composed of complex large molecules of polysaccharides, proteins and fats. The presence of lignocellulosic matter in OFMSW increases the hindrance to the process. Therefore, pretreatment of OFMSW before the AD process is recommended to (i) breakdown the complex substances into simpler ones, (ii) provide a large surface area and (iii) increase porosity to the substrate that increases the accessibility of food towards microorganisms. Different types of physical (Xu et al. 2016a, b), chemical (Bala et al. 2019), thermal (Li and Jin 2015), biological (Fdez-Güelfo et al. 2011a) and combinational pretreatment (Tyagi et al. 2014) strategies have been implied by researchers to increase the hydrolysis of OFMSW. However, little is known about the effect of biological pretreatments on OFMSW for biogas production.

In biological pretreatment, special bacterial and fungal strains capable of degrading complex matters are used to modify the substrate microscopic structure, to achieve improved biodegradability and high production yields. Some strains of white rot basidiomycetes, *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, *Cyathus stercolerus*, *Phlebia radiate*, etc. are capable of lignin degradation by the action of enzymes lignin peroxidase, manganese peroxidase and laccase (Rudakiya and Gupte 2017). The physico-chemical treatment followed by fungal (*Aspergillus terreus* and *Trichoderma viride)* treatment done on park waste resulted in a 22.7% increase in biogas yield (Ali and Sun 2015).

Thermo-chemical pretreatment is one of the widely applied methods to accomplish the AD requirements from different substrates. Thermo-chemical treatment generally applied in a low range of 60–120 °C and high-temperature range of 120–220 °C with a chemical reagent. NaOH-thermal treatment is an effective method for lignin degradation and organic matter solubilisation. NaOH primarily affects the main ether bonds (phenol type α-aryl ethers /α-alkyl ethers/β-aryl ethers/non-phenol type β-aryl ethers) present in lignin and also solubilise the glycosidic bonds between carbohydrate and lignin (Xu et al. 2016a, b). Breakdown of lignin makes the cellulose and hemicellulose vulnerable to microbial enzymes. The elevated temperature also showed a synergistic effect on biomass hydrolysis as revealed from the literature review. Thermal treatment at high temperature dissolves the cell membrane and drain the intracellular material into liquid. Despite the existence of some studies on OFMSW solubilisation by thermo-chemical treatment, the impact of this method on biogas production from OFMSW is still unknown. The best solubilisation conditions of OFMSW achieved for thermo-chemical treatment were 3 g/L NaOH, 180 °C and 3 bar pressure (Fdez-Güelfo et al. 2011b).

Response surface methodology (RSM) is a mathematical and statistical tool used to optimise the different variables of a process to achieve the best possible response (Zhang et al. 2018). Rodriguez et al. (2017) studied the optimisation of mechanical pretreatment of waste paper for biogas production. Safaria et al. (2018) optimised the co-digestion of canola residue and cow manure by RSM to increase biogas productivity in lab scale. Many researchers used RSM to optimise the sugar yield for enhanced saccharification for biofuel production (Aruwajoye et al. 2017; Kamalinia et al. 2018).

The present work is intended to analyse the effect of fungal pretreatment and NaOH-thermal pretreatment on OFMSW to achieve high OFMSW solubilisation for improved biogas yield. RSM model was applied to get optimised condition after selection of a narrow range of operating parameters of pretreatment. As previously mentioned, that effect of biological treatment on OFMSW is little known, so present work contributes in this regard. Also, the optimisation of a pretreatment through the RSM model provides more reliable results with less experimentation, less time and solvent consumption. To our knowledge, this type of software optimisation of the same pretreatment has not been done before on the same substrate.

Material and method

Substrate preparation and characterisation

MSW was collected from the dumping site of Varanasi. The biodegradable fraction was manually segregated. The OFMSW was washed and then ground to form slurry by adding some water and stored at 4 °C. The prepared slurry was characterised for proximate, ultimate values, pH, VFA and sCOD content. The inoculum for anaerobic digestion was effluent of biogas plant running on cow dung slurry situated at BHU, Varanasi. The physico-chemical characteristics of OFMSW and inoculum are depicted in Table 1. The experiments were carried out in duplicates, and the average value has been reported with standard deviation.

Biological solubilisation of OFMSW

Two strains of white rot fungi *Phanerochaete chrysosporium* and *Pleurotus ostreatus*, NCIM accession nos. 1197 and 1200 respectively, were acquired from National Collection of Industrial Microorganism (NCIM) Pune, Maharashtra, India. Fungal strains were maintained on potato dextrose agar (PDA) media composed of (per L) potato, 200 g; dextrose, 20 g; yeast extract, 0.1 g; and agar, 20 g at 28 °C for 10 days. The spore suspension was prepared from 4 fully grown Petri plates in sterilised conditions.

One hundred milliliters of OFMSW slurry was taken in a 250-ml conical flask and sterilised in an autoclave for 15 min, followed by 3 mL fungal spore inoculation and incubation at

Table 1 Physico-chemical characteristic of OFMSW slurry and inoculum

Properties (wt%)	OFMSW slurry	Inoculum
Proximate analysis		
Moisture content	90.7 ± 1.7	93.5 ± 1.6
Total solid	9.3 ± 1.7	6.6 ± 1.6
Volatile solid	8.2 ± 1.8	5.8 ± 1.5
Ultimate analysis$_{(db)}$		
Carbon	42.9 ± 3.1	39 ± 2.3
Hydrogen	5.9 ± 0.3	5.3 ± 1.2
Nitrogen	2.1 ± 0.2	3.4 ± 0.7
Oxygen	49.2 ± 3.3	52.3 ± 1.8
Chemical properties		
sCOD (mg /L)	15,652 ± 59.4	1908 ± 53.7
VFA (mg /L)	1731 ± 41	-
pH	6.8 ± 0.2	7.1 ± 0.1

db dry basis

28 °C for 5, 10 and 15 days with stirring at 130 rpm. After pretreatment time was over, it was centrifuged at 4500 rpm for 10 min, and the supernatant was separated to examine sCOD, VFA, glucose and phenolic content.

Thermo-chemical hydrolysis of OFMSW

Thermo-chemical hydrolysis of OFMSW was carried out at a varying concentration of NaOH in the range of 1–7 g/L, temperature (90–200 °C) and time (15–120 min). In the first experiment, the effect of different NaOH doses on OFMSW solubilisation was evaluated at 120 °C for 1 h. In the second set, the different temperature was tested with fixed NaOH dose of 5 g/L for 1 h, and in the third set, the effect of the varying time interval for hydrolysis was determined. Estimation of solubilisation parameters, sCOD, VFA and phenolic content was done after each pretreatment.

RSM optimisation of thermo-chemical treatment

The BBD design was generated by considering three main factors NaOH concentration, temperature and time interval of treatment; and sCOD, VFA and phenolic compounds as the response by using Design-Expert software version 7.0. The ranges of factors were determined according to the results of previously mentioned pretreatment experiments. The range of influencing factors was NaOH dose (3–6 g/L), temperature (150–180 °C) and time (30–90 min). The BBD design resulted in 17 experiments in random with 5 central replicates. The experimental data were fitted in the second-order polynomial equation (1) (Bezerra et al. 2008).

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

where Y denoted the predicted response, X_i and X_j denoted coded independent factors, β_0, β_i, β_{ii}, β_{ij} denoted constant regression coefficient, the coefficient for linear, quadratic and interaction terms respectively and ε denoted the residuals. ANOVA analysis was carried out to evaluate the significance of the model. The interactive effect of influencing factor was observed by generating 3-D plots.

Anaerobic digestion

The untreated and treated samples were undergone anaerobic digestion for biogas production in glass bottles of 500-ml capacity with a working volume of 350 ml. The reactor had two openings for nitrogen inlet and biogas outlet. It was equipped with a water displacement unit through a gas sampling tube. It was operated at 30 °C in batch mode with initial pH 7 and digestion period of 20 days. The substrate (g VS) to inoculum (g VS) ratio was adjusted as 0.5, and substrate loading was 5.5 g VS (3.31 g sCOD). Nitrogen gas was sparged for 5 min to maintain the anoxic condition inside the reactor. One control with only inoculum (cow dung) was operated in parallel to anaerobic digestion of treated and untreated samples. Biogas yield was corrected for the gas obtained from control.

Analytical techniques

Proximate analysis was performed using laboratory analytical procedures developed by the National Renewable Energy Laboratory (NREL). Carbon, nitrogen and hydrogen contents were measured by using automatic CHNS analyser (Euro Vector EA, Italy). sCOD was determined by an automatic sCOD analyser (UNIPHOS, India) after digesting the sample at 150 °C for 120 min in the presence of potassium dichromate, mercuric sulphate and sulphuric acid-silver sulphate reagent. VFA analysis was done by the titration method. The hydrolysate obtained from pretreatment was firstly titrated by 0.1 N HCl to get pH 4, then boiling of the sample was done for 3 min followed by titration with 0.01 N NaOH to reach pH 7. Volumes of NaOH and HCl were noted. The VFA content was calculated in terms of acetic acid (mg/L) by the following equation (Ziauddin and Rajesh 2015).

$$\mathrm{VFA}\left(\frac{\mathrm{mg}}{\mathrm{L}}\,\text{of acetic acid}\right) = 87.5 \times \text{vol of NaOH to reach pH 4–7} \qquad (2)$$

The reducing sugar measurement was done by using the DNS method by taking spectroscopic absorption at 540 nm wavelength (Miller 1959). Phenolic by-products estimation in terms of gallic acid was performed by Singleton's Folin-Ciocalteu reagent method by taking absorbance at 765 nm (Singleton and Rossi 1965).

A scanning electron microscope (SEM) (Zeiss evo 18 research, Germany) was employed to capture the surface structure of samples. Biogas volume was measured through the incorporation of water displacement column in experimental set up and biogas compositional analysis was carried out by gas chromatograph equipped with thermal conductivity detector (GC-TCD) (Nucon 5765) with N_2 as carrier gas at the flow rate of 30 ml/min and porapak Q (0.25 mm × 2 m) as separating column. The temperature of injector, oven and detector was 393, 363 and 393 K, respectively.

Result and discussion

Effect of biological treatment on OFMSW

Effect of *P. chrysosporium* and *P. ostreatus* on OFMSW solubilisation was studied, and findings are represented in Fig. 1. The concentration of sCOD and VFA were slightly increased with increasing the time of treatment. However, *P. chrysosporium* found to be more effective in improving the sCOD and VFA yield in comparison with *P. ostreatus*. Increment in sCOD and VFA value could be associated with the partial solubilisation of OFMSW sample. Hydrolysis of carbohydrates, protein and fats into sugar, amino acids and fatty acids may increase the sCOD concentration. Lignin reduction due to fungal pretreatment might have exposed the available cellulose and hemicellulose to microbes that in turn increased the soluble compounds and also sCOD value. The white rot fungal strains can cause degradation of lignin by secreting some lignolytic enzymes like lignin peroxidase, manganese peroxidase and laccase. The complete degradation of the lignin molecule takes place in fungal treatment due to the action of fungal enzymes without generation of the phenolic compounds. It is an advantage over other pretreatment methods like chemical pretreatment, where generation of the phenolic compound takes place with increasing degradation of lignin. The glucose and phenolic content yields were slightly decreased after pretreatment (Fig. 1c). The reduction in glucose yield might have associated with its consump-

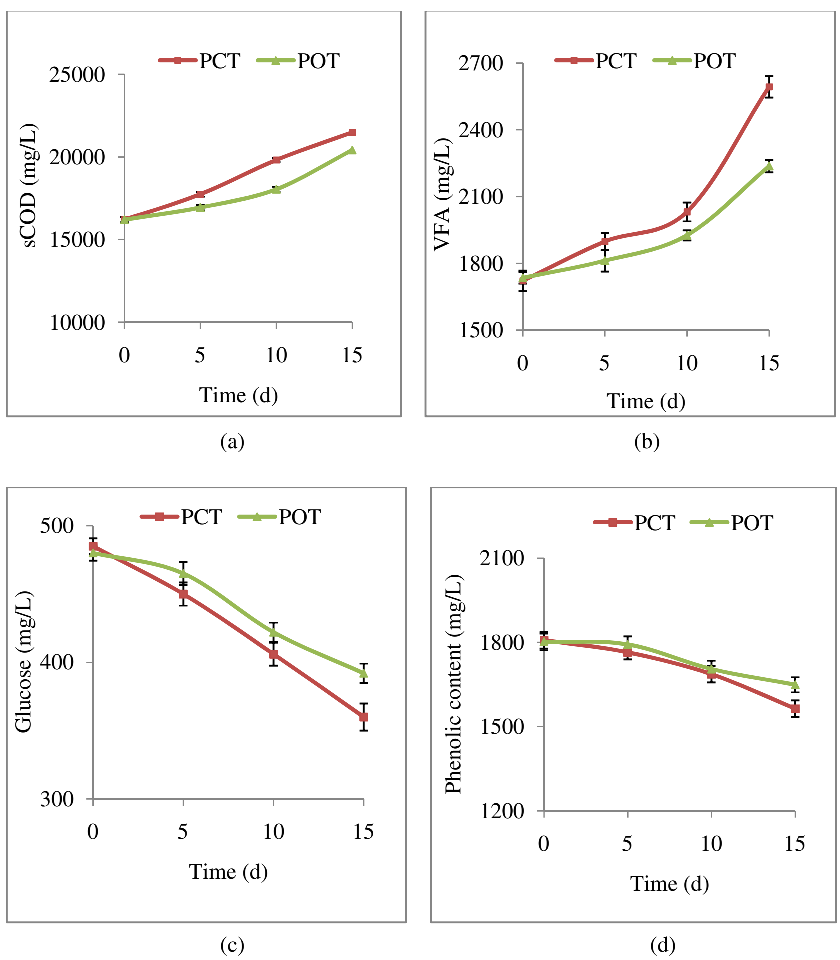


Fig. 1 Effect of biological pretreatment by *P.chrysosporium* (PCT) and *P. ostreatus* (POT) on OFMSW solubilisation (**a**) sCOD (**b**) VFA and (**c**) glucose and (**d**) phenolic content

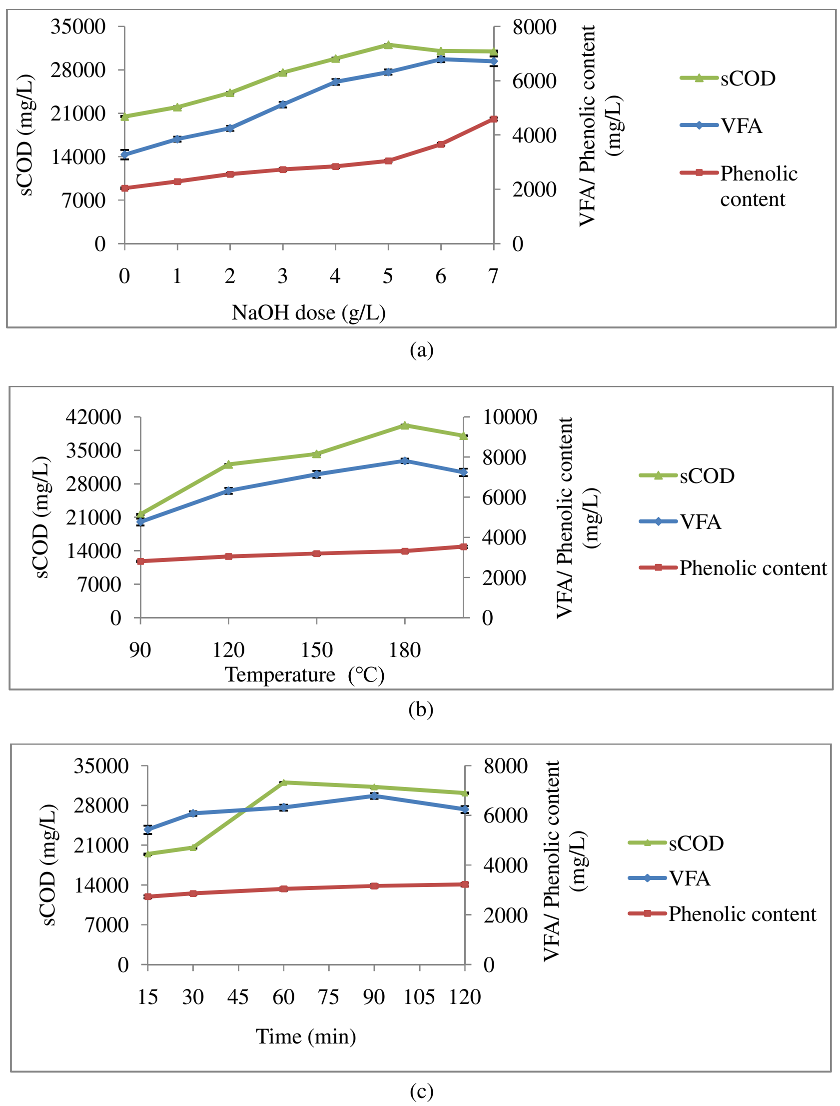
tion by microorganisms to fulfil their energy requirement, and phenol degradation was caused by fungal enzymes secreted by *P. chrysosporium* and *P. ostreatus*. The *P. chrysosporium* and *P. ostreatus* treatment have been widely applied to degrade the lignocellulosic material by researchers. The effect of such type of pretreatment on OFMSW has not been reported in the literature as per our knowledge. However, fungal strain *Aspergillus awamori* was employed by Fdez-Güelfo et al. (2011b) to solubilise the OFMSW.

Effect of thermo-chemical treatment

The NaOH dose significantly increased the sCOD, VFA and phenolic content, as shown in Fig. 2a. sCOD and VFA values were found to be approximately constant after 6 g/L NaOH dose. NaOH and thermal treatment carried out the conversion of complex compounds to simpler one by changing the surface structure and dissolving the cell membrane. Elevated sCOD and VFA yield signified the effect of pretreatment. NaOH performed saponification and solvation reaction causing uronic acid substitution on the side chains of hemicelluloses and cleavage of main ether bonds in lignin, ester and glycosidic bonds in cellulose, hemicellulose and lignin (Xu et al. 2016a, b). The other reactions in alkaline pretreatment that occur are breakdown of C–C bond, condensation and methylation. The C–C bond is very stable when present between aryl-aryl groups; it is breakable in aryl-alkyl or alkyl-alkyl and can reduce the size of the lignin molecule (Xu et al. 2016a, b). Degradation of lignin led to the production of phenolic by-products. Therefore, the phenolic content was increased by raising the NaOH concentration.

Besides the cleavage of lignocellulosic complex, NaOH might have caused denaturation of protein into small peptides and amino acids. In alkaline medium, the stability of the tertiary structure of protein might have decreased that led to breaking down of intermolecular hydrogen bonding. The

Fig. 2 Effect of thermo-chemical treatment (**a**) NaOH dose (**b**) temperature and (**c**) time on OFMSW solubilisation in terms of sCOD, VFA and phenolic content



hydrolysis of the peptide bond might happen due to the presence of high temperature and NaOH. Also, the lipids are converted into fatty acids during pretreatment.

The temperature was also found to have an important role in solubilising the OFMSW slurry. The sCOD and VFA yields were increased up to 180 °C, and then it was slightly decreased (Fig. 2b). The peeling and hydrolysis reactions of NaOH takes place at high temperature (> 140 °C) that causes swelling of the substrate and degrade carbohydrates into small sugar moieties. The reduction of sCOD and VFA beyond 180 °C is associated with thermal decomposition and caramelisation process at high temperature that can result in sugar degradation and less solubilisation yield (Álvarez-Gallego et al. 2015).

Effect of the time period of treatment is represented in Fig. 2c. The sCOD and VFA yields were increased up to 60 and 90 min of the treatment period, respectively. The decrease of sCOD and VFA occurred at a higher time period due to reduced efficiency of NaOH at longer times. The phenolic compounds increased slightly concerning NaOH concentration, temperature and time period.

Solubilisation yield of OFMSW was better in thermo-chemical treatment in comparison with biological treatment. Therefore, thermo-chemical treatment was optimised for better results. The effect of pretreatment factors on solubilisation parameters was concluded, and their narrow range was decided for RSM optimisation. The range selected was NaOH dose (3–6 g/L), temperature (150–180 °C) and time (30–90 min).

RSM optimisation

sCOD and VFA are important parameters to evaluate the pretreatment effect. During the hydrolysis process, the conversion of complex compounds into simpler molecules takes place that raises the sCOD and VFA concentration. These molecules are utilised by microorganisms for their metabolic needs and biogas formation. Therefore, increased solubilisation yield can be associated with increased sCOD and VFA values. Also, the increased solubilisation of lignin causes the formation of phenolic compounds into hydrolysate. Phenolic compounds are considered as inhibitory to microbial growth (Wirth et al. 2015). Therefore, to optimise the thermo-chemical treatment sCOD, VFA and phenolic compounds were taken under consideration.

The Box-Behnken design was generated by considering NaOH dose pretreatment temperature and time as potential influencing factors with the help of Design-Expert version 7.0 software. Maximisation of sCOD and VFA yields and minimisation of phenolic compounds were taken as an optimal response. Summary of obtained responses according to the 17 experiments suggested by BBD design are depicted in Table 2. The experiments were done in duplicates, and the average value was reported in the design matrix.

Model fitting and variance analysis

Experimental data were fitted into a quadratic model. C (NaOH dose), T (temperature) and t (time) are the coded influencing factors of pretreatment. The correlation equations for responses obtained were:

$$\mathrm{sCOD}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) = 30718 + 2202\,C + 4348.75\,T + 3333\,t - 648.5\,CT - 1193.5\,Ct - 4695\,Tt + 7407.25\,C^2 + 3651.25\,T^2 - 2466.7\,t^2 \tag{4}$$

$$\mathrm{VFA}\ (\mathrm{mg/L}) = 8026.6 + 913\,C + 776.13\,T + 81.13\,t + 328\,CT - 66.5\,Ct - 126.75\,Tt - 751.68\,C^2 - 483.43\,T^2 + 277.58\,t^2 \tag{5}$$

$$\text{Phenolic content}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) = 3542.4 + 480.75\,C + 202.38\,T + 242.88\,t + 85.25\,CT - 26.75\,Ct + 38\,Tt + 337.05\,C^2 - 330.7\,T^2 + 106.3\,t^2 \tag{6}$$

Model adequacy was checked by ANOVA analysis. The value of regression coefficients, R^2 for sCOD, VFA, and phenolic content were 0.9693, 0.9857 and 0.993, respectively (Table 3). The high R^2 values signified the adequate model fitting. Also, a model is considered as significant if its P value is less than 0.05 (Saha et al. 2018). The P value for all the responses was less than 0.05, indicating the statistical acceptance of the model. The F value is the test comparing the source's mean square to the residual mean square. The F value for sCOD, VFA and phenolic content was 24.55, 53.53 and 110.33, respectively. The significant terms obtained for sCOD were C, T, t, Tt, C^2, T^2 and t^2. Values greater than 0.1 considered as non-significant terms. C, T, CT, C^2, T^2 and t^2 were the significant terms for VFA and C, T, t, CT, C^2, T^2 and t^2 were the significant terms for phenolic content. The value of predicted R^2 was in good agreement with adjacent R^2 for all the responses. The values of predicted R^2 for sCOD, VFA and phenolic content were 0.7884, 0.7984 and 0.9052 and the values of adjacent R^2 were 0.9298, 0.9673 and 0.9840, respectively. Adequate precision indicates the signal to noise ratio. Its value greater than 4 is desirable (Zhang et al. 2011). The value of adequate precision 20.787, 24.344 and 38.230 for sCOD, VFA and phenolic content, respectively indicated the model adequacy. The coefficient of variance (C.V value) is the standard deviation expressed as a percentage of the mean. Its value less than 10% is considered significant. The C.V value for sCOD, VFA and phenolic content was 5.08, 2.39 and 1.68, respectively signified the model accuracy.

Effect of influencing factors on OFMSW solubilisation

The interacting effect of three variables NaOH dose, temperature and time were studied on multiple responses (sCOD,

Table 2 Box-Behnken design matrix for variables and responses

Run	*C*: NaOH dose (g/L)	*T*: temperature (°C)	*t*: time (min)	sCOD (mg/L)	VFA (mg/L)	Phenolic content (mg/L)
1	4.5	180	30	38,965	8635	3276
2	4.5	165	60	33,780	8143	3547
3	4.5	150	30	19,205	7021	2914
4	6	165	90	40,310	8657	4747
5	4.5	165	60	31,010	8010	3512
6	4.5	180	90	35,210	8367	3798
7	3	165	90	38,704	6787	3750
8	3	150	60	35,208	5423	3012
9	3	165	30	28,620	6315	3171
10	3	180	60	43,530	6511	3213
11	4.5	165	60	29,880	8078	3572
12	6	180	60	47,048	8816	4256
13	4.5	165	60	29,930	7987	3505
14	6	150	60	41,320	6416	3714
15	4.5	165	60	28,990	7915	3576
16	6	165	30	35,000	8451	4275
17	4.5	150	90	34,230	7260	3284

VFA and phenolic content) using RSM methodology. The 3-D contours were generated to compare the effect of factors and optimise the pretreatment conditions. Figure 3 represents the effect of influencing factors on response.

The sCOD, VFA and phenolic content yields were increased with respect to NaOH dose and time. The rise in NaOH dose and temperature induced the breakdown of complex compounds raising sCOD, VFA and phenolic content. The interacting effect of temperature and time on responses is represented in Fig. 3d, e and f. The sCOD and VFA values were found to be more dependent on temperature in comparison with time. The sCOD and VFA content was increased up to 60 min and then further increment in time reduced their yield. The low phenolic content was desirable, and it was found at treatment done at low temperature for less time period. The interacting effect of NaOH dose and time is shown in Fig. 3g, h and i. The sCOD value was found maximum in two zones (Fig. 3g), i.e. it was increased for low NaOH dose and the increased time period and in the second case at high NaOH dose and less time period. Increasing the time period at high concentration might have induced the formation of VFA and other compounds that resulted in less sCOD yield. VFA and phenolic content were increased by increasing the NaOH dose and time period.

Model validation

The optimised condition for thermo-chemical treatment of OFMSW using RSM was NaOH dose 4.72, temperature 180 °C and time 30.3 min. The experiment at this condition was done in duplicate to verify the accuracy of the model. The experimental results were compared with predicted values of responses, and the error% is summarised in Table 4. The model was fitted with an error of 0.6, 1 and 0.7% for sCOD, VFA and phenolic content, respectively.

Table 3 Model fitting and analysis of variance

ANOVA parameter	sCOD	VFA	Phenolic content
Model suggested	Quadratic	Quadratic	Quadratic
F value	24.55	53.53	110.33
P value	0.0002	0.0001	0.0001
Significant terms	$C, T, t, CT, C^2, T^2, t^2$	C, T, CT, C^2, T^2, t^2	$C, T, t, CT, C^2, T^2, t^2$
R-squared	0.9693	0.9857	0.9930
Adj *R*-squared	0.9298	0.9673	0.9840
Pred *R*-squared	0.7884	0.7984	0.9052
C.V	5.08	2.39	1.68

Surface microscopic study of treated and untreated OFMSW

The surface structure of untreated OFMSW was rigid and intact, giving it a smooth surface, whereas the treated OFMSW found to have a fragile and disrupted surface (Fig. 4). The effect of *P. chrysosporium* treatment was visible by SEM images. Effect of *P. ostreatus* treatment was not so significant in OFMSW structure modification. The thermo-chemical treatment was found to be more potential to alter the OFMSW structure due to degradation of carbohydrate, protein and fat.

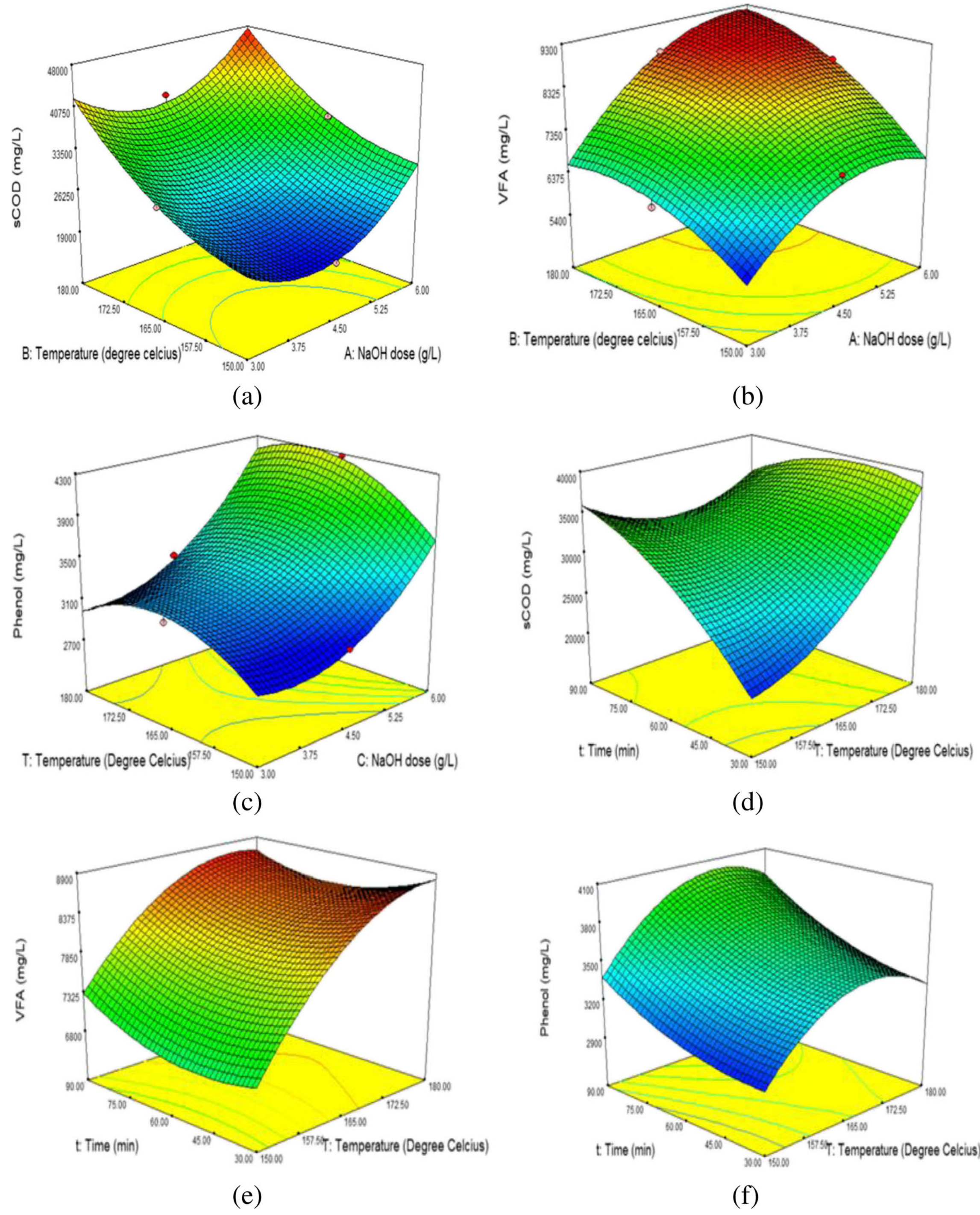


Fig. 3 RSM optimisation of thermo-chemical treatment, (**a**–**c**) effect of NaOH dose and temperature, (**d**–**f**) effect of temperature and time and (**g**–**i**) effect of NaOH dose and time on sCOD, VFA and phenolic content

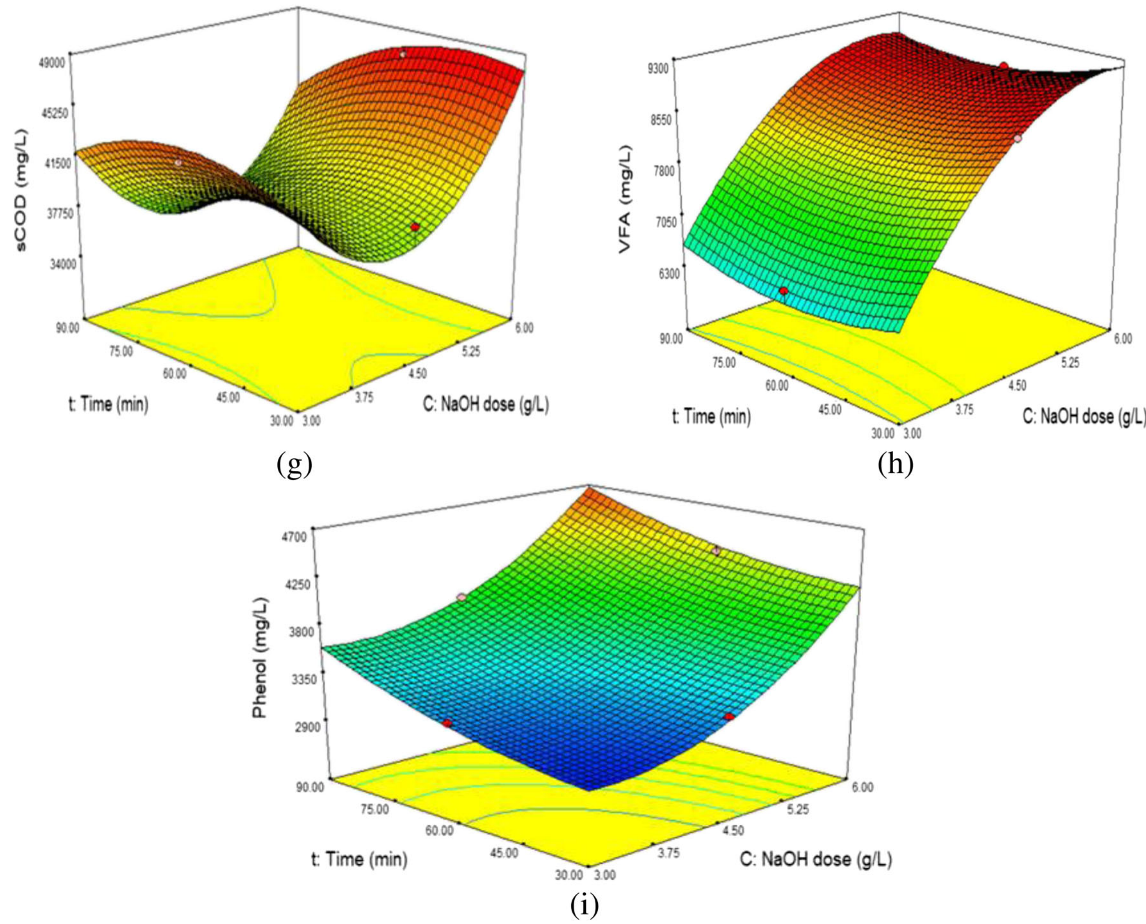


Fig. 3 (continued)

Anaerobic digestion

The results of biogas production are represented in Fig. 5. The results of biogas production are in accordance with the solubilisation of OFMSW. The presence of lignin in OFMSW makes the microorganism inaccessible to the substrate. As previously mentioned, strains of white rot fungi are capable of degrading lignin by using their ligninolytic enzymes. The *P. chrysosporium* treatment (PCT) might have degraded the lignin more efficiently than *P. ostreatus* (POT) and turned out in 13.9% more biogas production. The biogas was produced at a slow rate in POT and PCT treatment due to less availability of dissolved organic matter. Biological treatment slightly increased the biogas production (43.1%) in comparison with untreated OFMSW. However, thermo-chemical treatment at optimised condition (OTCT) resulted in an increment of 88.4 and 169.5% biogas production as compared with PCT and untreated OFMSW, respectively. Thermo-chemical treatment resulted in efficient solubilisation of organic matter present in OFMSW in terms of sCOD, VFA and phenolic content and significantly augmented the biogas production rate and cumulative biogas yield. The biogas production occurred with the fast rate in the first 10 days of digestion period in thermo-chemically treated samples. The digestion period of anaerobic digestion of thermo-chemically treated samples was also reduced due to breaking down of complex material during the pretreatment step. The methanogenesis rate is dependent on the hydrolysis of the substrate. Pretreatment

Table 4 RSM model validation

	NaOH dose (g/L)	Temperature (°C)	Time (min)	sCOD (mg/L)	VFA (mg/L)	Phenolic content (mg/L)
Predicted	4.72	180	30.3	38,221.6	8816	3336.46
Experimental	4.72	180	30	38,451	8728	3360
Error (%)	–	–	–	0.6	1	0.7

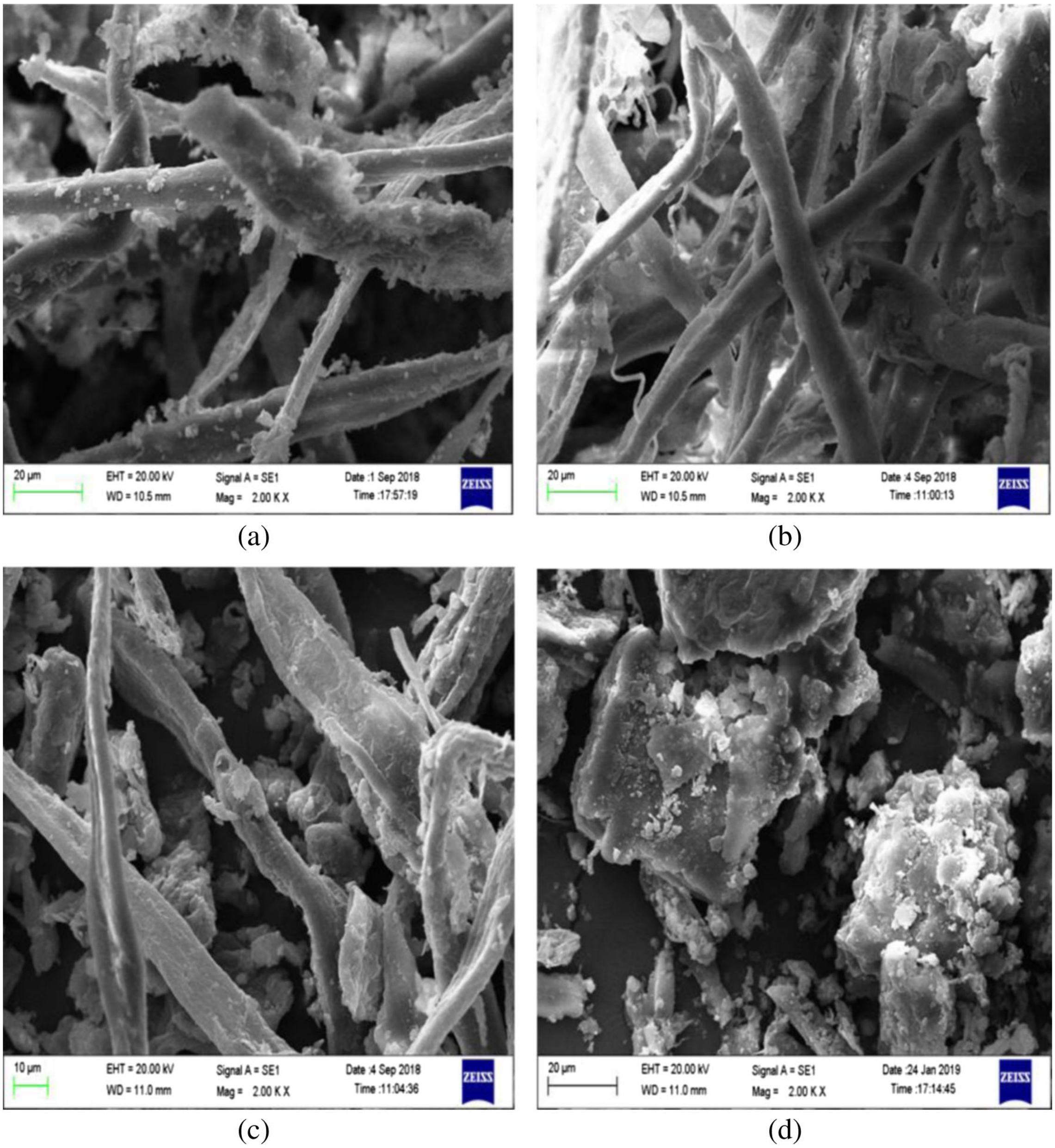
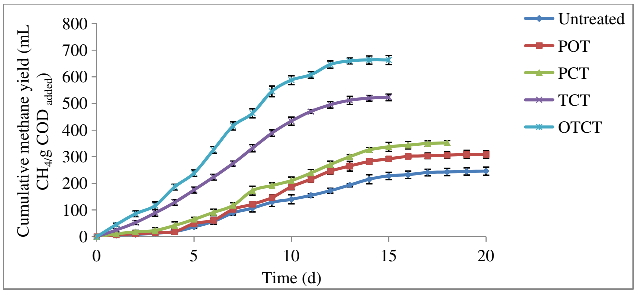


Fig. 4 Microscopic images captured by SEM (**a**) untreated, (**b**) *P. ostreatus* (POT), (**c**) *P. chrysosporium* (PCT) and (**d**) optimised thermo-chemical treatment (OTCT)

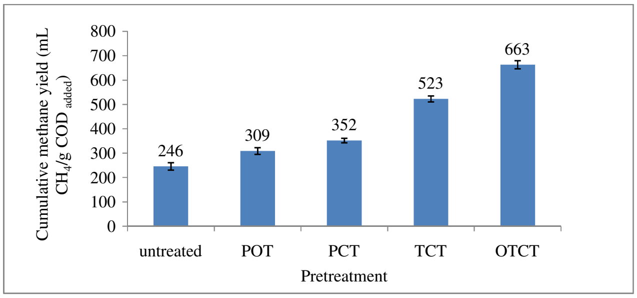
caused the dissolution of organic matter and increased the accessibility of microorganisms towards a substrate that resulted in better substrate utilisation and better biogas yield. The cumulative biogas production from untreated OFMSW was 246 ml CH_4/g COD $_{added}$. Biogas production from PCT, POT, TCT, and OTCT samples resulted in 352, 309, 523 and 663 mlCH_4/g COD $_{added}$ biogas, respectively. The biogas production was also increased (60%) when matured compost was used as biological treatment (Fdez-Güelfo et al. 2011a). The biogas production was increased by more than 50% of control at 170 °C with 4 g NaOH/100 g MSW (Wang et al. 2009). Methane concentration was found in the range of 61–64% in the biologically treated sample, whereas 66–70% for thermo-chemically treated sample. The difference in methane concentration might be due to the more solubilisation of OFMSW sample by thermo-chemical treatment in comparison with biological treatment.

Conclusion

P. chrysosporium was more effective than *P. ostreatus* in OFMSW solubilisation and biogas production. PCT resulted in 13.9% biogas improvement as compared with POT. TCT was best among all to enhance the solubilisation parameters, sCOD, VFA and phenolic content. TCT experiments indicated



(a)



(b)

Fig. 5 Biogas production at different conditions (**a**) cumulative biogas production profile and (**b**) comparison of biogas yield at different conditions

NaOH dose of 3–6 g/L, temperature 150–180 °C and 30–90 min time was an effective zone of OFMSW solubilisation. RSM optimised condition was achieved as 4.72 g/L NaOH dose, temperature 180 °C and time 30.3 min. Anaerobic digestion at OTCT resulted in 169.5% enhanced biogas yield as compared with untreated OFMSW. The optimisation of process parameters for anaerobic digestion can further study to enhance the biogas yield. The scale-up of the process from pretreatment to anaerobic digestion at pilot plant level can be done. The work can also be extended to biogas upgradation for methane enrichment.

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