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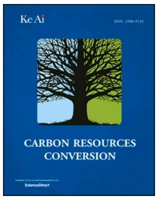

Effect of varying hydrothermal temperature, time, and sludge pH on sludge solubilisation

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A B S T R A C T

In recent years, hydrothermal treatment has been considered as among the most promising option for sludge solubilisation and carbon recovery in terms of sludge management. In this study, the effect of different individual hydrothermal operating conditions like temperature (110–250 °C), sludge pH (6–13) and reaction time (0.5–3 h) were varied to understand their influence on sludge solubilisation. The most effective hydrothermal conditions (severity factor of 9.7) were found to be at 200 °C, sludge pH of 12 and reaction time of 1 h which solubilised about 1743 mg/g and 131 mg/g of COD and carbohydrates respectively into the aqueous phase. Also, gas chromatography- mass spectrometry (GC–MS) analysis was done that identified the organic compounds in the treated liquid phase to be mainly carboxylic acids, phenols, esters, and their derivatives. Although further studies are required to efficiently separate and recover the different organic compounds present, this work provides more insights for future valorisation of the organic rich hydrothermally treated liquid phase.

1. Introduction

Waste sludge is the nutrient rich biological material produced as surplus from a biological reactor [1]. When it is produced by an activated sludge process in the wastewater treatment, it is referred to as waste activated sludge (WAS). The excess of sludge is removed from the activated biological sludge process to keep the desired ratio between the organic substrate and the biomass in the biological reactor. The waste sludge contains high concentration of microorganisms, basically bacteria, protozoa and fungi aggregated as flocs. From the chemical point of view the sludge is mainly composed of proteins, carbohydrates, and humus that can be usefully utilised as a source of biodegradable renewable matter [2]. However, these organic molecules are present in a complex matrix in the sludge flocs [3]. It is therefore necessary to break the floc structure and open the microbial cell walls and membranes to facilitate solubilisation and release of the components and molecules which than can be recovered or eventually converted into other interesting molecules [4]. Among the several different techniques employed to enhance sludge solubilisation, thermal hydrolysis is considered to be a feasible choice as it destroys microorganisms and aids with reduction of sludge volume which is considered beneficial from the point of view of the wastewater treatment processes [5]. This last point is highly relevant for the management of wastewater treatment plants since the high volume of waste sludge generated yearly consistently affects the economy of the wastewater facilities and the environment [6]. Nevertheless, really high-water content of over 95 % in waste activated sludge can hinder the effective application of standard thermal methods [7].

However, in recent years, hydrothermal treatment which is a particular kind of thermal method has been gaining attention [8]. It uses hot pressurised water as both reactant and solvent without causing secondary pollution [9]. Hydrothermal method can be classified based on the operating temperature: hydrothermal carbonization at 180–250 °C, hydrothermal liquefaction at 250–400 °C and super critical water gasification at temperatures above 400 °C [10]. Hydrothermal carbonization converts biomass to solid fuels while liquefaction produces biofuels [11]. For hydrothermal gasification below 600 °C, methane is the major product and above 600 °C, hydrogen rich gaseous products can be recovered [12]. In addition to generation of energy products from dewatered sludge, hydrothermal treatments also improve anaerobic digestion process to produce biogas from sludge that has not been dewatered [13].

Hydrothermal methods are gaining increasing interest among the researchers as it can be observed from Fig. 1 through a search on the Scopus database. Nevertheless, this technology is still not enough

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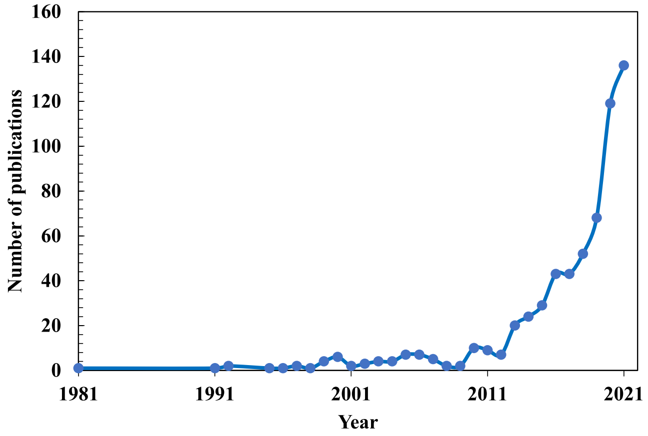

Fig. 1. Number of publications indexed by Scopus with the query “hydrothermal AND waste AND sludge” in the fields title, abstract and keywords.

mature for a wide application on an industrial scale and further studies are still necessary to address its features, characteristics of the products, applicability, strength, and weakness on the different types of sludges.

The process waters from hydrothermal carbonization are not often investigated as one of the important products of the hydrothermal process. The composition of the process waters is dependent on the type of sludge hydrolysed and on reaction parameters like temperature, time, sludge pH and ratio of dry solids to water. One of the most common applications of process waters is biogas production using digested sludge as starting material [14]. A recent review summarises the main studies reported by researchers on hydrothermal carbonization of anaerobically digested sewage sludge with focus on the chemical and physical properties of process waters [15]. The effect of process parameters investigated in this review were varied as: temperature 160–380 °C, time 20 min- 7 h, and pH 4.7–10.0. Only very few works in literature examined the effect of varying reaction conditions on the properties of process waters obtained from carbonization of sludge before digestion for their applications other than biogas production. Munsik Park et al studied the effect of hydrothermal conditions 150–300 °C, 0.5–3 h, sludge concentration 5–30 g/L to determine the optimal parameters for WAS solubilisation by analysing the disintegration degree and concentration of dissolved organics in the process waters [16]. Whereas Liqun Xiao et al used the process waters of WAS after microwave hydrothermal treatment for 5-hydroxymethylfurfural (HMF) production by varying parameters of temperature 200–230 °C, time 5–30 min, pH 0.5–4 [17].

However, a thorough research of relevant literature did not find any specific works examining the individual effect of temperature 110–250 °C, pH 6–13, and reaction time 0.5–3 h on the characteristics of process waters of WAS done in a single study. This work is done in continuation to the author’s previous study in order to improve the severity of WAS pre-treatment conditions to enhance organics solubilisation in the process waters [18]. Chemical oxygen demand (COD) and carbohydrates on the filtered samples were measured to determine the best operating parameters for sludge solubilisation and identification of the solubilised organic compounds. This knowledge would be valuable for developing alternate pathways for valorisation of hydrothermally treated WAS samples apart from production of biogas and also for subsequent related research.

2. Material and methods

2.1. Materials

Waste activated sludge (WAS) used in this study was collected from the oxidation tank of a municipal wastewater treatment plant in Genoa, Italy. Some chemical properties of WAS have been determined. The raw sludge sample contains 5.0 g/L of total solids (TS) (measured on as received basis), 4.0 g/L of volatile solids (VS) (measured on dry basis) and 1.0 g/L of mineral solids (measured as difference and on dry basis). Additionally, it had chemical oxygen demand (COD) and carbohydrates concentrations of 500 mg/L and 140 mg/L respectively (both measured on the liquid fraction of WAS) and a pH ~ 6.0. The sludge was preserved at 4 °C to prevent any degradation till it was used for the batch experiments. Chemicals such as sodium hydroxide (NaOH) used for pH variation and ethyl acetate were purchased from Sigma Aldrich and used as received.

2.2. Batch hydrothermal treatments

Prior to the hydrothermal tests, sludge was thickened by decantation to biomass concentration of 11.5 g/L (measured on wet basis), volatile solids of 9.2 g/L (dry basis). Hydrothermal treatments of activated sludge were performed as batch experiments using a stainless-steel reactor of maximum capacity of 12 ml and varying treatment conditions. The effect of individual hydrothermal conditions was studied by varying the parameters as follows: temperature of 110–250 °C; pH of 6–13; and reaction time of 0.5–3 h. The treatments with an alkaline pH were carried out using 5 M NaOH to set the initial pH of the thickened WAS to the desired pH. Alkaline pH range was selected here as it was found to improve sludge solubilisation according to our previous work [18]. Initially, about 8 ml of concentrated sludge was loaded into the reactor and purged with nitrogen gas for 3 mins. The autoclave was then heated in a ventilated oven as per the desired operating temperature. After the set reaction time of experiment, the autoclave was removed from the oven and cooled using water to room temperature. The treated sludge sample was filtered with a 0.2 μm polyether sulfone syringe filter (Merck, Darmstadt, Germany) to separate the organic rich liquid and solid fraction.

Severity factor log ($R_o^{''}$) is a parameter that is used to show the combined effect of treatment temperature, retention time and pH in a single factor as expressed by Eq. (1) [19]. This equation gives a better comparison of the severities of hydrothermal treatments performed at different pH conditions.

$$\log(R_o^{''}) = \log(R_o) + |\mathrm{pH} - 7| \tag{1}$$

where R_o is a factor that integrates the effect of temperature and time period of treatment as calculated using Eq. (2).

$$R_o = t.exp\left(\frac{T(t) - 100}{14.75}\right) \tag{2}$$

where t is the retention time in min, T(t) is the treatment temperature (°C), 100 is the reference temperature (°C), and 14.75 is the constant value often used based on the activation energy when pseudo first order kinetics is assumed.

2.3. Sample analyses

Merck Spectroquant analytical cell test kit (catalog number 114,541 from Darmstadt, Germany) was used to measure soluble chemical oxygen demand (COD). The soluble carbohydrates were determined by Dubois’s colorimetric phenol–sulfuric acid method with D-glucose as standard solution for calibration [20]. Sludge pH was measured using a pH 209 bench top pH meter (Hanna Instruments Italia, Ronchi di Villafranca Padovana, Italy). The composition of the soluble compounds in the liquid fraction was expressed as mg/g and was calculated by dividing the concentration of soluble parameter (mg/L) with concentration of thickened sludge (g/L). All the experiments were carried out in duplicates, and the results were expressed as means ± standard deviation.

The liquid fraction of the treated sample was subjected to gas chromatography-mass spectrometry (GC–MS) analysis. The sample was extracted with ethyl acetate in a 1:1 vol ratio after acidifying it to pH 2 with a hydrochloric acid solution (37 %). The extracted liquid was dehydrated with sodium sulphate salt and filtered before injection into a gas chromatography-mass spectrometry (Shimadzu GCMS-QP2010 SE) system equipped with an HI-5 MS column (Avantor Hichrom, 30 m × 0.25 mm × 0.25 µm). Acetone was used as the solvent for cleaning the syringe of the autosampler and helium (1 ml/min) was the carrier gas. The injection port and ion source temperatures were 250 °C and 200 °C, respectively. The solvent cut time was 2.5 min. The GC oven program was as follows: 60 °C held for 3 min, with a linear temperature gradient of 25 °C/min to 300 °C and held for 4 min. 1 µL of sample was injected with a split ratio of 20:1. Data acquisition was in full scan mode in the *m/z* range from 35 to 700 amu. The peaks in the spectra were identified using a NIST (National Institute of Standards and Technology) library associated with the instrument and only the peaks with a similarity of above 70 % are reported here.

To understand the effect of severity of hydrothermal treatments on solubilisation of soluble compounds, the Pearson's correlation coefficient (R) was applied to determine linear correlations between these two parameters. R value is always between −1 and +1 and they represent a perfect negative correlation and a perfect positive correlation respectively while 0 denotes the absence of a correlation between parameters. Correlations were considered statistically significant at a 95 % confidence interval ($p < 0.05$).

3. Results and discussions

Hydrothermal parameters such as temperature, pH and reaction time were found to influence the solubilisation of sludge [21,22]. Between 130 and 270 °C, hydrothermal treatments have been found to show enhanced performance for both primary and secondary sludges from wastewater treatment plants [23]. At temperatures below 210 °C, the release of several types of monomers (e.g., oligo and monosaccharides, proteins and amino acids, fatty acids) through a dissolution mechanism is expected [24]. Alkaline hydrothermal treatments have been previously studied to destroy sludge floc and cell structure [25]. The damage to the sludge microbial structures enhanced the solubilistaion of the organic matter present in WAS [26]. Although different alkalis like sodium hydroxide, potassium hydroxide, calcium hydroxide and magnesium hydroxide have been utilised for alkaline treatment, it is sodium hydroxide addition that provides highest rate of solubilisation and is most used [27]. The effect of hydrothermal treatments by varying the individual operating parameters on the solubilisation of organics was done here. The thickened sludge used had a biomass concentration of 11.5 g/L and vS of 9.2 g/L. Initially only one reaction condition was changed, and other parameters kept constant. The effect of the different hydrothermal conditions on sludge solubilisation was studied by evaluating the concentrations of soluble COD and total carbohydrates.

3.1. Effect of varying hydrothermal temperature

Fig. 2 shows the results obtained at different temperatures for a reaction time of 1 h and it can be seen that soluble organic compounds like carbohydrates were released as a result of hydrothermal treatments. The pH of the samples was not altered and was measured to be 6.0 before the hydrothermal runs. Untreated sludge had COD and carbohydrates concentrations of 43 mg/g and 12 mg/g respectively. Increasing the temperature, increased the COD concentration from 147 mg/g at 110 °C to a maximum of 1022 mg/g at 250 °C. Generally using COD measurements, it is difficult to accurately calculate the concentration of soluble organics due to the interference from several inorganic ions like chlorides and ammonium that are present in the soluble phase [28]. However, COD content provides a preliminary information on the influence of hydrothermal treatments on sludge solubilisation. In the past, COD has been used as a simple measurable variable for determining organic concentration in the absence of other analytic instruments [16,29]. Furthermore, carbohydrates concentration was also measured that helped to supply some additional information on the solubilisation of organics by hydrothermal treatments. The carbohydrate content increased from 73 mg/g at 75 °C to 95 mg/g at 250 °C.

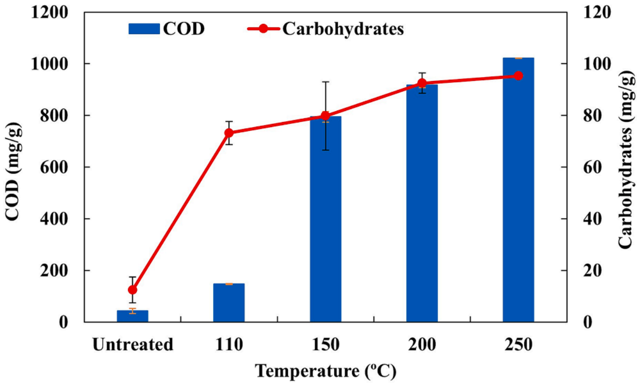

Fig. 2. Composition of soluble chemical oxygen demand (COD) and carbohydrates at different temperature between 110 and 250 °C.

The ideal operating temperature depends on the type of sludge and its properties. In this case, as temperature increased from 110 °C to 200 °C, the increase in COD was almost six times, which further improved only slightly as temperature reached 250 °C. A similar behaviour was shown by total carbohydrates results. The above results indicate that the temperature range of interest in terms of COD and carbohydrates is between 150 and 250 °C.

3.2. Effect of varying sludge pH

From results shown in Fig. 2, best temperature range was selected as 150–250 °C. Therefore, for this temperature range, pH was changed using NaOH addition in the range from 10 to 13 for an operation time of 1 h in the hydrothermal reactor. Alkaline pH conditions were chosen based on previous studies which indicate that in basic environment the biomass matrix is better disintegrated [18]. Hydrothermal tests were performed at 150, 200, and 250 °C as shown in Fig. 3.

At 150 °C, as the pH increased even the COD contents increased to a maximum value of 1626 mg/g at pH 13 from 795 mg/g at pH 6. The solubilisation of COD was largely improved from pH 12 and above. Carbohydrate concentration was enhanced from 80 mg/g at pH 6 to 144 mg/ g at pH 13 and showed an increasing trend similar to that of COD.

The COD of the untreated sludge of 43 mg/g increased to 917 mg/g at 200 °C for sample at pH 6. Adding NaOH increased the COD content further to a maximum value of 1743 mg/g at pH 12 which decreased on increasing the pH to 13 and above. A similar trend was also observed in the case of carbohydrates released with concentration increasing 10 times from 12 mg/g for untreated sample to 131 mg/g for hydrothermal treatment at pH 12 which was reduced to 104 mg/g at pH 13.

The COD solubilisation trend at hydrothermal temperature of 250 °C was in the increasing order and similar to that at 150 °C. At pH 12, COD released improved significantly to 1495 mg/g while increasing the pH further to 13 enhanced the COD contents only by a smaller concentration to 1595 mg/g. Soluble carbohydrate concentration was elevated to 112 mg/g at pH 12 from 95 mg/g at pH 6. However, at pH 13 there was a drop in the carbohydrate content to 104 mg/g and this behaviour was similar to that at 200 °C. A probable reasoning for this could be the degradation of carbohydrates to other organic molecules at more severe treatment conditions of pH 13 and temperatures of 200 °C and higher.

The organic matter in WAS is mainly comprised of 40 % proteins, 25 % lipids and 15 % polysaccharides [21]. COD solubilisation is due to the decomposition of carbohydrates, proteins, lipids to smaller molecules like simple sugars, amino acids, and fatty acids [30]. At the different temperature conditions, values of COD and carbohydrates were improved at alkaline pH conditions as compared to sludge treatments at

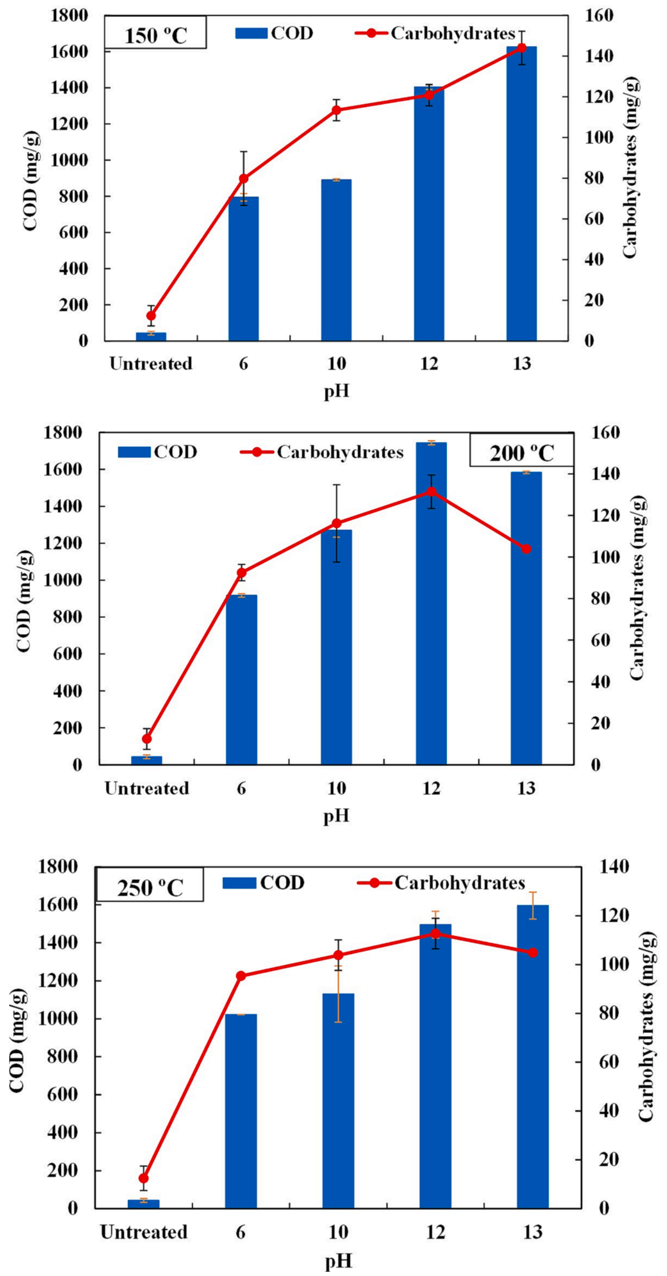

Fig. 3. Impact of pH on solubilisation of COD and carbohydrates at 150 °C, 200 °C and 250 °C.

pH 6 which could be attributed to microbial cell lysis in addition to sludge floc lysis at higher pH [3]. During hydrothermal treatment, proteins get converted to smaller peptides that further decompose into amino acids while polysaccharides like cellulose convert to simple sugars like glucose [31]. It is easier to break down carbohydrates in comparison to proteins during hydrothermal carbonization [32]. So, at lower temperatures and pH the COD solubilisation could be contributed from carbohydrates decomposition and at higher temperatures and more alkaline pH conditions, it could be due to protein degradation. However, at 200 °C and pH 13, the drop in COD values could be because of the availability of the glucose from carbohydrate decomposition that interact with amino acids to form Maillard reaction that hinders with COD solubilisation as reported previously [32]. Also, Dogan & Sanin reported that pH 11 microbial cell damage is much lower than at pH 12–12.5 [33]. This agrees with our results, where below pH 12 the improvement in COD and carbohydrates solubilisation is lower for all the operating temperatures than at pH 12 and higher. Hence, from Fig. 3 it can be seen that an alkaline pH is optimum to open the biomass matrix and the optimal conditions to maximize COD and carbohydrates were 200 °C and pH 12.

Additionally, titration experiments were done on sludge using 1 M NaOH solution and compared with MQ water as shown in Fig. 4. In this case, buffer capacity was calculated as number of moles of a base added per litre of sludge to influence pH [34]. The sludge was found to have a buffer capacity of 0.00588 mol/L/pH unit as shown in Fig. 5 and to reach pH 12 from the starting sludge pH of 6, it was necessary to add 1.7 ml of 1 M NaOH to 50 ml sludge whereas, MQ water required 1.1 ml of the same NaOH solution to bring its pH to 12. It could be suggested from the titration curves that the sludge behaved as a weak acid due to the probable presence of volatile fatty acids.

3.3. Effect of varying hydrothermal reaction time

From the previous experimental runs, 200 °C was chosen to be the best temperature and 12 to be the best pH in terms of highest concentrations of COD and carbohydrates that were released into the aqueous phase of sludge after hydrothermal treatments. At these best identified conditions, the effect of reaction time on sludge solubilization was studied in the range 0.5–3 h as it was the final parameter selected in addition to temperature and pH affecting solubilisation. Also, to better understand the results, hydrothermal treatments at pH 6 and 200 °C were also performed. Fig. 6 shows the influence of reaction time on solubilisation of COD and carbohydrates at pH 6 and 12. It can be observed that at pH 6, there was an increase in COD from 766 to 1013 mg/g from 0.5 to 3 h while in case of carbohydrates, the increase was from 80 to 93 mg/g from 0.5 to 1 h and lowered to 83 mg/g after 3 h. There was an increasing trend at pH 12 in terms of COD content from 1548 to 1826 mg/g. Carbohydrate concentration increased 131 mg/g at 1 h which dropped to 120 mg/g after 3 h. This behaviour was same at pH 6 and 12. A possible reasoning could be as hydrothermal treatment progresses there is solubilisation of organics including carbohydrates and also simultaneous decomposition of these dissolved organics into other compounds and it agrees with previous work as reported by Yin et al [35].

Regarding reaction time, solubilisation of organics mainly takes place at the initial period of hydrothermal carbonization for both pH 6 and 12 as compared to untreated sludge and a similar trend was reported by Pola et al [36]. As time progresses, soluble COD increases for both pH values as seen in Fig. 6. It was reported in the past that solubilisation of organics at alkaline conditions take place in two stages, a first fast stage at 0.5 h followed by a slower stage [37]. In the initial phase, the weakly bound dispersible sludge floc is degraded while at the subsequent phase, the tightly bound stable part of sludge structure is disintegrated over time [38]. So, this could be the reason for increase in COD values at both pH while soluble carbohydrates concentration dropped after 1 h of

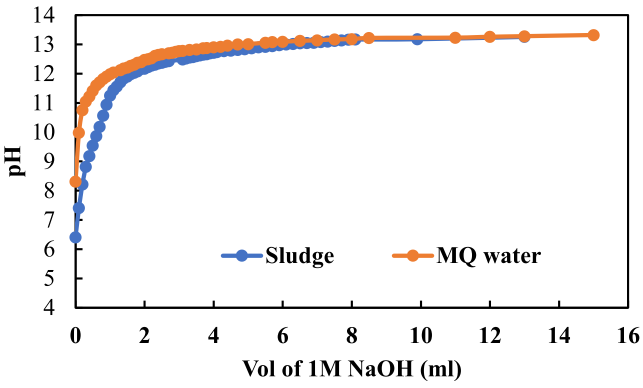

Fig. 4. Titration curves for sludge and MQ water using 1 M NaOH solution.

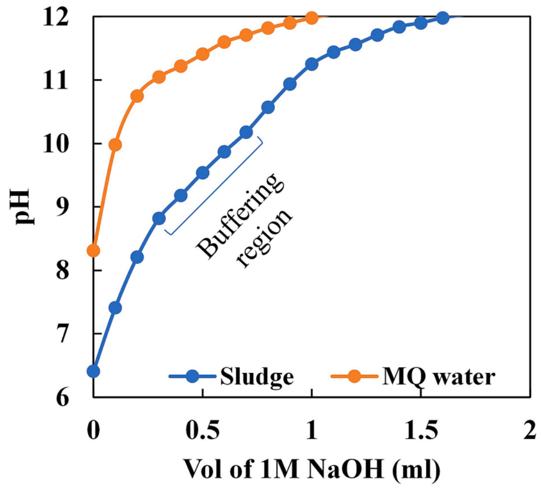

Fig. 5. Determination of buffer capacity of sludge.

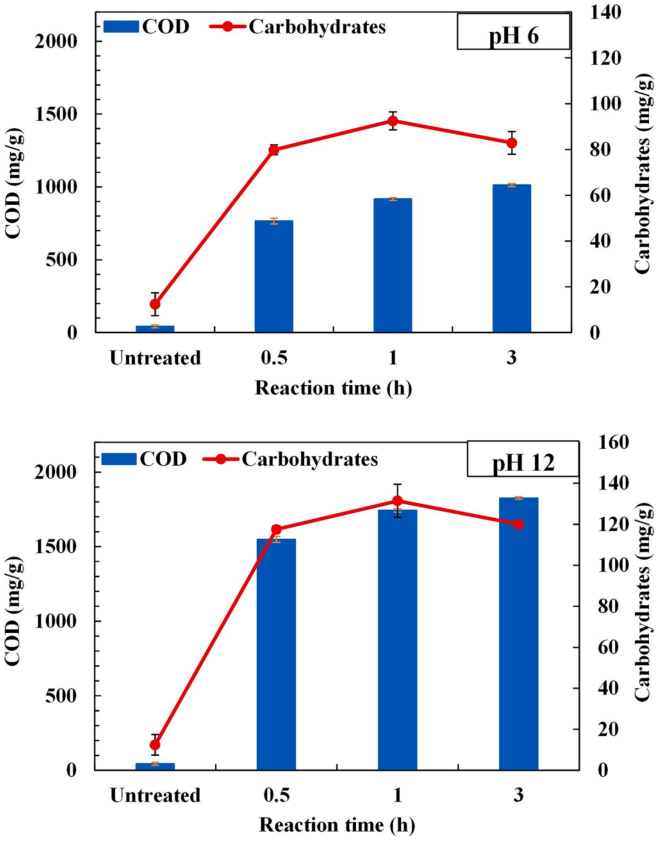

Fig. 6. Impact of reaction time on solubilisation of sludge at 200 °C and pH 6 and 12.

reaction.

All of the above reactions are done on a small scale using a reactor of 12 ml capacity. It is therefore necessary to upscale the treatments to better understand the behaviour of solubilisation of organics on varying the process parameters and on the heat transfer conditions. The results of COD and carbohydrates obtained in this study were compared with previous works using stainless steel reactors of bigger sizes to hydrolyse WAS. Batch experiments done in 300 ml reactor yielded a maximum COD of 258 mg/g at 300 °C and carbohydrates of 42 mg/g at 250 °C after 1 h of treatment at the original pH of WAS [16]. These values are much lower than the ones measured in this paper corresponding to the respective treatment conditions. However, hydrothermal treatment done in a one litre PARR reactor at 160 °C, 40 bar, 1 h and no pH variation resulted in COD of about 10–12 g/L and carbohydrates of 1–1.5 g/L [39]. The values are quite comparable to COD and carbohydrates obtained in this work at 200 °C for 1 h of reaction and pH 6. One of the drawbacks of hydrothermal carbonization is that most findings assume the reaction temperature to be constant. Meanwhile, a batch hydrothermal reaction involves a time to heat up, residence time and time for cooling down. So, the comparison of results from similar works is difficult as the results achieved will be dependent on the actual experimental conditions and characteristics of the raw sludge utilised.

3.4. *Severity of treatments vs solubilisation of organics*

Table 1 gives the values of severity factor for different treatments when varying the reaction temperature, time, and pH. Fig. 7 explains the Pearson correlation between the COD and carbohydrates measured with the severity factor $\log\left(R_o''\right)$ calculated using equation (1). It can be observed that severity of 7.2 and above resulted in COD solubilisation of more than 1000 mg/g. This was achieved at lower temperature of 150 °C at higher pH of 12 or greater. Whereas, at 200 °C, even a lower pH of 10 made this possible and at highest temperature of 250 °C, pH 6 gave this value of severity. It can be seen that improving the temperature and pH of reaction, greatly enhanced COD as compared to longer retention time. Finally, severity factor of 9.7 was found to be the best in terms of COD solubilisation and increasing the severity beyond this value negatively affects the solubilisation process. This trend was also noticed in past literature, where higher intensity of hydrothermal carbonisation adversely affected the dissolution of COD [32]. In case of soluble carbohydrates, increasing hydrothermal severity had a considerable effect and as temperature increased and with no change in pH, concentration of carbohydrates released also improved. However, at temperatures of 200 °C and above and at pH 13, this value was found to be lowered. Also, increasing the reaction time to 3 h at 200 °C, a similar trend was observed. The optimum severity factor for carbohydrates solubilisation was at 9.3 and beyond this value, the concentration of carbohydrates dropped. This enhancement of solubilised carbohydrates up to a certain severity factor could be because of the degradation of the higher molecular weight polysaccharides to smaller weight molecules like simple sugars and increasing the severity to above this range could further decompose it into VFAs thereby reducing the total carbohydrates measured which agrees with previous works [40,41]. After the different hydrothermal treatments, it can be seen from Fig. 7, that there is a very high positive correlation ($R = 0.91$, $p < 0.05$) between soluble COD and severity factor which indicates that enhancing the severity of treatment

Table 1
Severities of different hydrothermal treatments when varying the process parameters.

Temperature °C	Time h	pH	$\log(R_o'')$
110	1	6	3.1
150	1	6	4.3
150	1	10	6.3
150	1	12	8.3
150	1	13	9.3
200	0.5	6	5.4
200	1	6	5.7
200	3	6	6.2
200	1	10	7.7
200	0.5	12	9.4
200	1	12	9.7
200	3	12	10.2
200	1	13	10.7
250	1	6	7.2
250	1	10	9.2
250	1	12	11.2
250	1	13	12.2

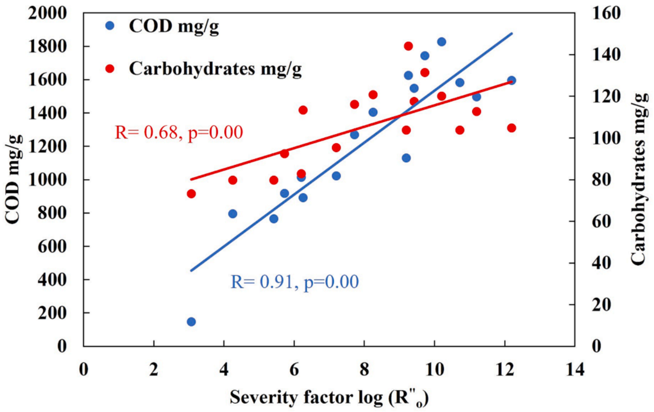

Fig. 7. Pearson correlation between solubilised COD and carbohydrates with severity factor.

significantly improves solubilisation of organics. While soluble carbohydrates and severity have a positive moderate correlation (R = 0.68, $p < 0.05$) suggesting that increasing severity only has a mild effect on solubilisation of carbohydrates. Overall, it can be concluded that improving the severity of reaction up to a certain range is important for the dissolution of organic compounds.

3.5. GC–MS analysis of solubilised liquid

The organic compounds extracted by ethyl acetate from the liquid fraction of hydrothermally treated sample at 200 °C, pH 12 and reaction time of 1 h were determined by gas chromatograph equipped with a mass spectrometer detector. This particular sample was selected for GC–MS as it gave the best results in terms of COD and carbohydrates solubilisation. The peak area percentages of the main compounds with a similarity percentage of above 70 are given in Table 2. After analysing the GC–MS results, the main organic matter in the liquid is found to be phenolics, ester and acids. Alkaline treatment enhances the hydrolysis of macromolecules like carbohydrates, lipids, proteins in sludge. They are hydrolysed to their monomeric units like glucose, long chain fatty acids and amino acids [42]. The decomposition of fatty acids and proteins resulted in the formation of volatile fatty acids (VFAs) like butanoic acid, butanoic acid, 3-methyl-, heptanoic acid, and pentanoic acid, 4-methyl- as reported in Table 2. Also, it can be observed that about 50–60 % of the peak area here is related to organic fatty acids and their derivatives like 1,4-benzenedicarboxylic acid, bis(2-ethylhexyl) ester, pentanoic acid, 4-oxo-, 2,4-dimethylpentanoic acid, octanoic acid, undecanoic acid, formic acid, 4-methoxyphenyl ester, and VFAs. This could be due to the fact there is higher concentration of proteins in sludge as compared to other classes of organics [43,44]. Hence at alkaline pH, there is hydrolysis of proteins and decarboxylation of amino acids resulting in higher fraction of fatty acids and some amines like N-(2-aminoethyl)-*N*-methylethylenediamine. Also, alcohols like 1,2-ethanediol, monoacetate, and 1-octanol, 2-methyl- that are found could be the products of decarboxylation and hydrodeoxygenation of fatty acids present [45,46]. Carbohydrates present get hydrolysed to reducing sugars like glucose, fructose, xylose that decompose to 5-hydroxymethylfurfural and furfural [47]. These degradation products could be converted to formic and levulinic acid by rehydration [48]. This could explain the presence of pentanoic acid, 4-oxo- also known as levulinic acid in the GC–MS results. By-products of the above reaction route could be multiple compounds like phenolics, alcohols, VFAs, and monomers of carbohydrates, proteins, and lipids [49]. Major composition of phenolics in Table 2 like phenol, 2,2′-methylenebis[6-(1,1-dimethylethyl)-4-methyl-, and p-cresol could be attributed to this. Also, the absence of reducing sugars in GC–MS results indicate that hydrothermal carbonization at temperature of 200 °C was high enough to completely disintegrate them as agreed by previous authors [50].

Table 2
Peak area and similarity percentages of the compounds in the solubilised liquid.

Compound	Area %	Similarity %
Phenol, 2,2′-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	34.8	90
1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	13.1	82
Butanoic acid	9.5	84
Pentanoic acid, 4-oxo-	8.4	88
Butanoic acid, 3-methyl-	6.9	86
p-Cresol	5.1	89
Heptanoic acid	4.4	78
2,4-Dimethylpentanoic acid	3.7	82
Pentanoic acid, 4-methyl-	2.8	83
Octanoic acid	2.6	79
Undecanoic acid	2.5	74
Formic Acid, 4-methoxyphenyl ester	1.9	74
1,2-Ethanediol, monoacetate	1.8	80
N-(2-Aminoethyl)-*N*-methylethylenediamine	1.7	71
1-Octanol, 2-methyl-	0.8	77

All the products obtained can be valuable if recovered. As an example, we will just mention the applications of the most abundant molecules. The main organic product identified phenol, 2,2′-methylenebis[6-(1,1-dimethylethyl)-4-methyl- is commercially known as an antioxidant from the group of bisphenols which can be used as antiaging agent in the polymer and rubber industry [51]. 1,4-benzenedicarboxylic acid, bis(2-ethylhexyl) ester as well as butanoic acid can find applications in coating products, adhesives, and sealants [52]. Furthermore, pentanoic acid, 4-oxo- (levulinic acid) is a well-known and widely studied green platform molecule [53,54].

4. Conclusions

The work was focused on the screening of hydrothermal process conditions for enhanced solubilisation of waste activated sludge using batch hydrothermal reactions. The impact on sludge solubilisation was evaluated by examining the soluble COD and carbohydrates concentrations in the treated aqueous phase of sludge. The effect of reaction temperature, pH and time was studied individually. All the parameters had a significant influence on sludge solubilisation and the best values were obtained at temperatures between 150 and 200 °C, alkaline pH and reaction time of 1 h. The best results obtained for COD and carbohydrate solubilisation were 1743 mg/g and 131 mg/g respectively at 200 °C, pH 12 and 1 h. Here, the effect of different hydrothermal treatment conditions on WAS solubilization was evaluated which is the first step for a biorefinery exploiting sludge as a resource. The treatments resulted in increase of the concentration of dissolved organics with the most efficient treatment being in alkaline medium. Gas chromatography-mass spectrometry results on the solubilised aqueous part of the hydrothermally treated sample showed the presence of larger fractions of organic acids and phenols and their derivatives from the hydrolysis of sludge proteins and carbohydrates in alkaline media. Suggested further work would be scale up of the hydrothermal treatment and the valorisation of this potential liquid phase including selective separation and recovery of the different molecules to be used as either primary or secondary raw materials for the production of bio-chemicals or value-added molecules.

CRediT authorship contribution statement

Reshma Babu: Investigation, Validation, Formal analysis, Writing – original draft, Visualization. **Gustavo Capannelli:** Supervision, Resources, Writing – review & editing. **Massimo Bernardini:** Investigation. **Marcello Pagliero:** Resources, Writing – review & editing. **Antonio Comite:** Conceptualization, Methodology, Data curation, Writing – review & editing.

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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