

## Article

# Understanding the Influence of Diverse Non-Volatile Media on Rheological Properties of Thermophilic Biological Sludge and Evaluation of Its Thixotropic Behaviour

Maria Cristina Collivignarelli <sup>1,2</sup>, Sara Todeschini <sup>1,2</sup>, Stefano Bellazzi <sup>1</sup>, Marco Carnevale Miino <sup>1,\*</sup>,  
Francesca Maria Caccamo <sup>1</sup>, Silvia Calatroni <sup>1</sup>, Marco Baldi <sup>3</sup> and Sauro Manenti <sup>1,2</sup>

<sup>1</sup> Department of Civil Engineering and Architecture, University of Pavia, Via Ferrata 3, 27100 Pavia, Italy; mcristina.collivignarelli@unipv.it (M.C.C.); sara.todeschini@unipv.it (S.T.); stefano.bellazzi01@universitadipavia.it (S.B.); francescamaria.caccamo01@universitadipavia.it (F.M.C.); silvia.calatroni01@universitadipavia.it (S.C.); sauro.manenti@unipv.it (S.M.)

<sup>2</sup> Interdepartmental Centre for Water Research, University of Pavia, Via Ferrata 3, 27100 Pavia, Italy

<sup>3</sup> Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100 Pavia, Italy; marco.baldi@unipv.it

\* Correspondence: marco.carnevalemiino01@universitadipavia.it

**Abstract:** In this study, the rheological properties of thermophilic biological sludge (TBS) have been investigated evaluating the influence of non-volatile solids (NVS). Calcium carbonate, sand, and sodium bentonite were separately added to the sludge to evaluate the effect of concentration and type of NVS. Results show that TBS consistency coefficient significantly enhanced increasing sodium bentonite concentration. On the contrary, calcium carbonate and sand showed relatively small influence on the rheological properties of TBS. Thixotropic behaviour of TBS has also been investigated and is more pronounced at higher shear rate ( $1000 \text{ s}^{-1}$ ). Double exponential fitting model was the best choice to represent thixotropic behaviour in case of low ( $100 \text{ s}^{-1}$ ) and high shear rate ( $1000 \text{ s}^{-1}$ ), while a single-exponential model represents the best option in case of medium shear rate ( $400 \text{ s}^{-1}$ ).

**Keywords:** thermophilic sludge; non-volatile solids; sewage sludge; rheology; sludge conditioning; thixotropic behaviour

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## 1. Introduction

Knowledge of the rheological properties of biological sludge (BS) is essential for optimizing the management of a high-strength wastewater treatment plant for several aspects: (i) membrane performance [1], energy consumption (e.g., in sludge pumping), hydrodynamics of bioreactors [2], oxygen transfer by aeration systems [3], and sludge sedimentation [4].

The hydrodynamic behaviour of the BS is closely related to its characteristics, which include the relative concentration of solids, the nature of the wastewaters and the treatment process to which it is subjected. At low concentrations of total solids (TS), the sludge behaviour can be reasonably approximated in most cases as a Newtonian fluid with a linear relationship between shear stress and strain rate and negligible yield stress [5]. Therefore, measured viscosity is rather independent of the shear rate at given temperature and pressure values, and the flow curve is represented by a straight line. As the concentration of TS increases, the sludge deviates from the Newtonian behaviour and can assume shear-thinning or shear-thickening behaviour. For such a non-Newtonian sludge the measured viscosity becomes dependent on the shear rate and the ratio of shear stress to shear rate, so-called apparent viscosity, is introduced [6]. The rheological

characterization of non-Newtonian sludge leads to practical difficulties in interpreting the behaviour of mixed liquor. The Ostwald–de Waele model, the Bingham model, the Herschel and Buckley model, and the Casson model are most commonly used to express non-Newtonian relationships between shear stress and shear rate for activated sludge. They can provide a suitable description of the sludge properties for practical applications [7].

Several studies have shown that temperature significantly influences rheological characteristics [6,8]. For instance, Baroutian et al. [6] studied the dependence of the rheological properties of a BS on temperature in a range from 25 °C to 55 °C, finding a reduction of the viscosity value with increasing temperature. As already described in the literature, the rheological parameters of a sludge depend upon other process parameters such as pH [9,10], TS concentration, [11,12], and volatile solids (VS) concentration [13]. Treatments to which the sludge is subjected also influence the rheological properties. Several differences have been reported in the literature between non-digested mesophilic sludge [9,14], digested mesophilic sludge [14,15], and thermal hydrolysed sludge [14,16]. For instance, digestion influences the rheological properties reducing viscosity of BS due to VS degradation [9,14,15]. Also thermal hydrolysis processes can lead to a reduction of the consistency coefficient of BS thanks to the breaking of the long chains of fatty acids inside the sludge [14,16]. These differences highlight how those processes to which the BS is subjected can strongly influence its rheological behaviour. In spite of how the knowledge that the rheological behaviour of BS is increasing, most of the studies were conducted in mesophilic conditions—though thermophilic sludge can also be used to biologically treat high strength wastewaters. With high temperature conditions (T: 45–48 °C), a biomass was selected that had several advantages such as a higher degradation rate of the organic substrate, lower excess sludge production and rapid inactivation of pathogens [17]. However, as a drawback, thermophilic biological sludges (TBS) have poor settling properties which make it necessary to couple membranes in case of operation with high biomass concentration [18].

Data on the rheological properties of TBS are limited to the influence of temperature and TS, without focusing, for example, on non-volatile solids (NVS). Furthermore, the modelling of the thixotropic behaviour of a TBS represents a new topic in the international scientific panorama. In the technical literature relatively few studies have been found linking shear stress and time in a deterministic way [19–22].

This work aims to study how diverse types and concentrations of NVS affect the rheological properties of a complex biological substrate such as TBS. Understanding the influence of diverse types of NVS on the rheology of TBS represents a key point to reliably characterize the hydrodynamic behaviour of the matrix. Furthermore, the time–response of TBS was investigated for applied shear stress to evaluate and characterize the thixotropic properties. The investigation approach and obtained data aim at providing practical information for facility managers to deal with practical problems occurring during the treatment process while assuring suitable levels of the plant efficiency.

## 2. Materials and Methods

### 2.1. Thermophilic Biological Sludge (TBS)

TBS was sampled in a full-scale membrane reactor fed with high-strength wastewaters. Thermophilic biological reactor operated at a temperature of almost 48–50 °C and was followed by ultrafiltration membranes for sludge separation. Details about the full-scale thermophilic membrane reactor configurations are reported in our previous study [23]. After sampling, TBS was delivered to the laboratory in a plastic tank within 1 h to preserve the biological activity and qualitative properties of the sludge. The main characteristics of the unconditioned sludge are reported in Table 1.

**Table 1.** Characteristics of unconditioned TBS. u.m.: unit of measure; (\*): calculated as a difference between TS and VS.

Parameter (u.m.)	Value	Analytical Method
<i>Rheological Properties</i>		
k (–)	0.012–0.22	–
n (–)	0.51–1.1	–
<i>Physico-Chemical Properties</i>		
pH (–)	7.5–8	[24]
TS (kg m <sup>−3</sup> )	175–185	[25]
VS (kg m <sup>−3</sup> )	85–95	[26]
NVS (kg m <sup>−3</sup> )	85–95	*
COD (mg L <sup>−1</sup> )	180,000–190,000	[27]
N <sub>tot</sub> (mg L <sup>−1</sup> )	4000–5000	[28]
P <sub>tot</sub> (mg L <sup>−1</sup> )	45–50	[29]
N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>−1</sup> )	150–160	[30]
N-NO <sub>3</sub> <sup>−</sup> (mg L <sup>−1</sup> )	250–300	[31]
N-NO <sub>2</sub> <sup>−</sup> (mg L <sup>−1</sup> )	40–55	[32]

## 2.2. Choice of Non-Volatile Media

The main aim of this work is to investigate the rheological properties of TBS during the operating conditions of existing treatment plants at full scale and how these properties can be affected by most frequent causes of malfunctioning in order to provide a useful dataset that can be of help for managers to adopt remedial measures and assure suitable plant efficiency levels. For this reason, it was decided to test three types of NVS species usually already present within a WWTP because the article aims to provide useful information to the operator of a thermophilic biological plant for the treatment of high-strength wastewaters. The non-volatile media tested were:

- Calcium carbonate, as it represents a residual product of the reaction of lime in water and is very frequently used in full-scale high-strength wastewater treatment plants;
- Sand, to understand if malfunctions of the sand removal processes, which result in a high number of solid particles entering the thermophilic biological reactor, can affect the rheology of the BS;
- Sodium bentonite, as it can limit the filtering properties of membranes. For this reason, understanding the influence of this substance in biological membrane processes is a fundamental aspect for the optimization of treatment.

## 2.3. Rheological Properties

### 2.3.1. Evaluation of Sludge Consistency

In literature, several mathematical models are available in order to describe the rheological properties of BS [33]. Most of these models adopt a power-law curve that includes an offset to account for the yield stress ( $\tau_0$ ). When considering thermophilic biological sludge from a membrane system [34], the Herschel–Buckley model (Equation (1)) [35] can provide an adequate representation of the experimental data because BS is characterized by a high concentration of solids [36]. Denoting with  $\tau$  the shear stress and with  $\dot{\gamma}$  the shear rate, the model reads:

$$\tau = \tau_0^{HB} + k\dot{\gamma}^n \quad (1)$$

where  $k$  and  $n$  represent the consistency coefficient and the flow behaviour index, respectively. When  $n$  equals to 1 a Newtonian behaviour is obtained,  $n$  lower than 1 indicates pseudoplastic properties, and  $n$  higher than 1 indicates a dilatant behaviour. The

more  $n$  differs from 1, the more fluid deviates from Newtonian properties.  $\tau_0^{HB}$  indicates the yield stress.

For every different dosage of diverse type of NVS, the estimated values  $k_i$  and  $n_i$  of Herschel–Buckley model were related to the corresponding parameters  $k_0$  and  $n_0$  of unconditioned sludge.

### 2.3.2. Evaluation of Thixotropic Behaviour

Three different models, referred to as single, double, and triple exponentials, were used to interpolate the measured shear stress values over time (Equations (2)–(4)) and were then compared to evaluate which one provides the best fitting to the experimental curve.

$$\tau = Ae^{-at} \quad (2)$$

$$\tau = Ae^{-at} + Be^{-\beta t} \quad (3)$$

$$\tau = Ae^{-at} + Be^{-\beta t} + Ce^{-\chi t} \quad (4)$$

### 2.4. Experimental Procedure

To evaluate the effect of increasing TS concentration on rheological behaviour, TBS was conditioned with calcium carbonate, sand, and sodium bentonite that were separately added. Calcium carbonate (particle size 1–3  $\mu\text{m}$ ) and sodium bentonite (particle size 35–105  $\mu\text{m}$ ) in powdered form were purchased (Heiltropfen, United Kingdom) while sand (particle size 0.16–0.24 mm) was sampled as a grit removal residue in a full-scale wastewater treatment plant (WWTP). Sand was washed with distilled water to avoid the presence of organic matter; it was subsequently dried at 105 °C in an oven (Memmert, Germany) to avoid the presence of water which could alter the test.

TBS was conditioned by adding NVS from 90 kg  $\text{m}^{-3}$  up to 190 kg  $\text{m}^{-3}$  of concentration. After that, the conditioned TBS was mixed for 4 h at 50–80 rpm to completely homogenize the sample before performing the rheological measurement. The value of VS, on the other hand, remained unchanged compared with the unconditioned sample.

Rheological tests were performed using RC20 coaxial cylinders rheometer (RheoTec, Germany) with a CC25DIN configuration (i.e., spindle radius 12.5 mm; stator internal radius 13.56 mm). The following shear rate values were tested: 25  $\text{s}^{-1}$ , 50  $\text{s}^{-1}$ , 100  $\text{s}^{-1}$ , 200  $\text{s}^{-1}$ , 400  $\text{s}^{-1}$ , 600  $\text{s}^{-1}$ , 800  $\text{s}^{-1}$ , and 1000  $\text{s}^{-1}$ . The experimental procedure to acquire data for evaluating the flow curve of the testing sludge sample was carried out by maintaining each shear rate value for 150 s before increasing it at the next measurement step. Shear stress and apparent viscosity were acquired every 15 s (i.e., ten datasets for each share rate step). The shear stress values measured at each time and plotted in the following figures should not be intended as instantaneous values as they represent the average of the measures taken within the corresponding sampling time interval of 15 s. The mean and confidence interval of the shear stress measurements were calculated for each applied shear rate. Moreover, before carrying out the shear stress measurement at different shear rate steps, each sludge sample was preliminary subjected to a fixed shear rate (i.e., 400  $\text{s}^{-1}$ ) for a constant time (i.e., 300 s) to cause structure breakdown and reduce the possible thixotropic influence on the rheological measurements.

In a subsequent step, to evaluate a possible thixotropic property of TBS, the shear stress and the apparent viscosity were recorded at three diverse shear rates (100  $\text{s}^{-1}$ , 400  $\text{s}^{-1}$ , and 1000  $\text{s}^{-1}$ ), each of which has been maintained for a suitably long-time interval (i.e., 1200 s). Shear rate values have been selected to provide an overview of the sludge behaviour within the investigated range. These values have been considered sufficient to obtain suitable information at this early stage of investigation, while the number of investigated shear rate values will be enhanced in subsequent studies.

It must be pointed out that other experimental techniques can be applied for the thixotropic analysis of a non-Newtonian fluid, such as the 3-intervals thixotropy test (3ITT) from the multiple interval thixotropic test protocol (miTT) [37]. The 3ITT test can be conveniently used for applying an instant shear stress/shear rate deformation in order to simulate effects of pumping and stirring during food processing [38]. In any case, common full-scale applications of TBS in wastewater treatment plants involve overall steady state operating conditions with negligible shear stress/shear rate mean local variations.

To reproduce full-scale operating conditions, the temperature during all tests was kept at  $48 \pm 2$  °C using a thermostatic bath (VELP Scientifica, Italy).

### 2.5. Data Processing

All parameters of Equation (1) were estimated by fitting the experimental data. The yield stress was considered as a deterministic parameter ranging in the interval (0–3.9 Pa) with steps of 0.05 Pa [36]. For each of these values, the coefficient of determination  $R^2$  was estimated for the measured shear stress–shear rate values. The yield stress that maximizes  $R^2$  has been assigned to the parameter  $\tau_0$  in Equation (1). The accuracy of the fitting of model was assessed through the standard estimation error. For each concentration (say  $i$ ) of NVS,  $k$  and  $n$  parameters of the Herschel–Buckley model were related to the corresponding parameters of the unconditioned sludge.

For the description of the thixotropic properties, the parameters of exponential models (Equations (2)–(4)) have been estimated with a non-linear least square constrained algorithm, as implemented by the *lsqcurvefit* function of Matlab®.

The parameter  $\Delta$  (Equation (5)) was used to compare fittings of different exponential models in diverse conditions.

$$\Delta = m_{line} - 1 \quad (5)$$

where  $m_{line}$  represents the coefficient of linear interpolation of model data as a function of experimental data. If  $\Delta$  is positive the model overestimates experimental data, and vice versa models were also compared using the Akaike's Information Criteria (AIC) index [39] (Equation (6)), which represents a method for evaluating and comparing statistical models. It is defined as:

$$AIC = 2p - 2\ln(L) \quad (6)$$

where  $p$  represents the number of parameters in the statistical model and  $L$  is the maximized value of the likelihood function of the estimated model. In this study, given the Gaussian distribution of the error,  $L$  has been considered equal to the sum of the normalized residues squared. The AIC index provides a measure of the quality of the estimate considering both the goodness of fit and the mathematical complexity of the model. Generally, models with the lowest AIC are preferred.

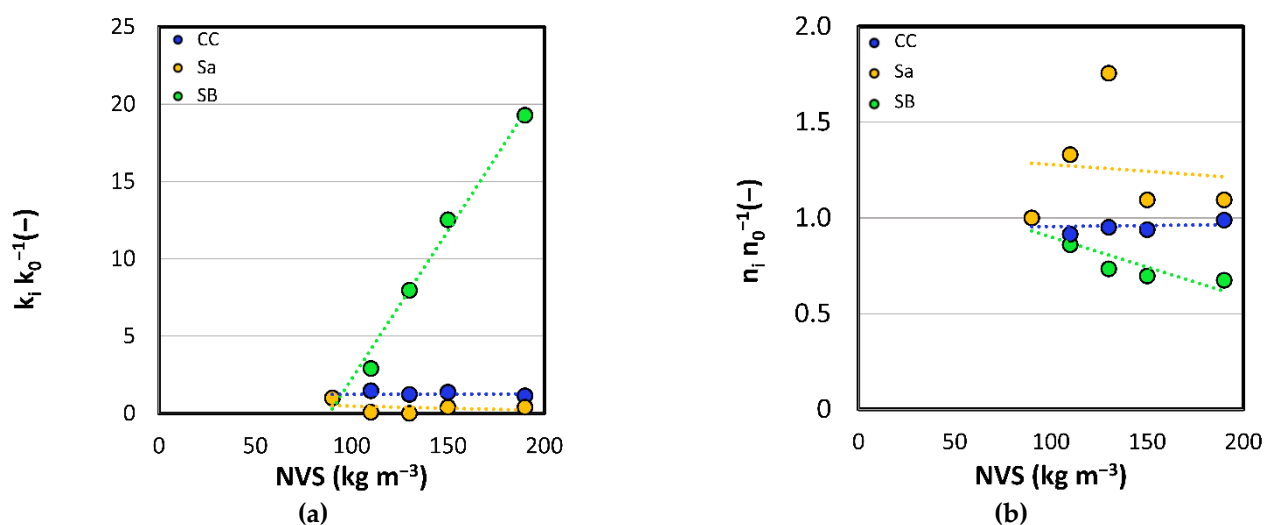
## 3. Results

### 3.1. Dependence of Rheological Parameters from Non-Volatile Media

Preliminary tests (see Supplementary Materials) highlighted how non-volatile media can potentially affect the rheological behaviour of TBS sampled in diverse reactors. Two TBS samples were extracted from two diverse full-scale plants (with similar conditions of feeding and operational temperature) and both the consistency coefficient, and the flow behaviour index were calculated to characterize the sludge from a rheological point of view. Results show that TBS with lower TS and NVS content exhibited a higher consistency coefficient, thus suggesting a possible relation between NVS and rheological properties.

Therefore, the influences of non-volatile media concentration and type were considered and the relation between these factors and TBS rheology was deeply studied. Figure

1 shows the results of the tests carried out by varying the concentration of diverse non-volatile media in TBS.



**Figure 1.** (a) Variation of consistency coefficient of conditioned TBS with respect to unconditioned sludge  $k_i k_0^{-1}$  as a function of NVS concentration. (b) Variation of flow behaviour index of conditioned TBS with respect to unconditioned sludge  $n_i n_0^{-1}$  as a function of NVS concentration. Dot lines represent the linear tendency. CC: calcium carbonate; Sa: sand; SB: sodium bentonite.

The consistency coefficient ( $k_i$ ) of the fluid conditioned with calcium carbonate was nearly constant despite a strong increase in the concentration of solids inside the tested sludge sample (Figure 1a). The variation of parameter  $k$  with respect to that of the unconditioned sample ( $k_0$ ) was expressed by the non-dimensional ratio  $k_i k_0^{-1}$  that reached 1.1. However, this increase was limited when compared with an increase in NVS concentration greater than 110% (from  $90 \text{ kg m}^{-3}$  to  $190 \text{ kg m}^{-3}$ ). Moreover,  $n_i n_0^{-1}$  also remained almost the same. It reduced from a value of 1 (unconditioned situation) to 0.98 at  $190 \text{ kg m}^{-3}$  concentration of NVS (Figure 1b), showing an almost negligible influence of this type of non-volatile media on the rheology of TBS within the investigated concentration range.

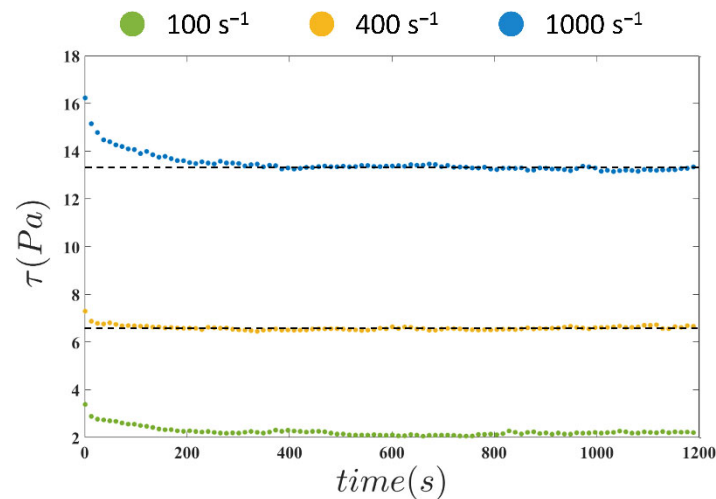
In the case where the sample was conditioned with sand, the sludge consistency coefficient reduced to 0.5 the value of the unconditioned sludge (Figure 1a). Apart from two values of the flow behaviour index  $n$ , obtained with NVS concentration in the range 120–140  $\text{kg m}^{-3}$ , deserving further investigation, the distance from the Newtonian behaviour was relatively small (i.e.,  $n_i n_0^{-1} \approx 1.1$ ) if compared with an increase in NVS concentration greater than 110% (Figure 1b).

Sodium bentonite produced the greatest influence on TBS rheology among the three types of NVS (see Supplementary Materials). Increasing NVS from the initial  $90 \text{ kg m}^{-3}$  up to  $190 \text{ kg m}^{-3}$ , the ratio  $k_i k_0^{-1}$  reached the value of 19.29 (Figure 1a). Concerning the flow behaviour index ( $n$ ), adding sodium bentonite made the conditioned sludge behave like a pseudoplastic fluid as the ratio  $n_i n_0^{-1}$  was always lower than 1 for all NVS concentrations, reaching the minimum value of about 0.67 at the highest NVS concentration (Figure 1b).

### 3.2. Evaluation of Sludge Response after Prolonged Imposed Shear Rate

In this case the experiment was aimed at investigating the possible thixotropic behaviour of a TBS unconditioned with a high solids content [40,41]. Tests were carried out on unconditioned sludge sample subjected to a constant shear rate for a duration of 1200 s. The thixotropic properties were evaluated for three shear rate values that are assumed to be representative of the sludge behaviour over a wide range of operating conditions:  $100 \text{ s}^{-1}$ ,  $400 \text{ s}^{-1}$ ,  $1000 \text{ s}^{-1}$ .

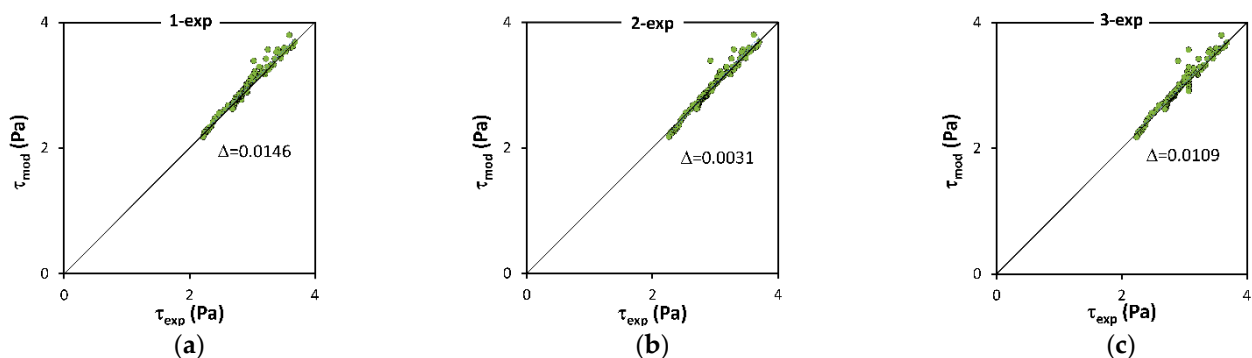
The experimental values of the shear stress  $\tau$  as a function of the time  $t$  are presented in Figure 2. As previously pointed out, the shear stress value plotted at each time represents the average measure within the corresponding time interval of 15 s which was assumed to be long enough to smooth out transient effects due to a change in the spindle rotation.

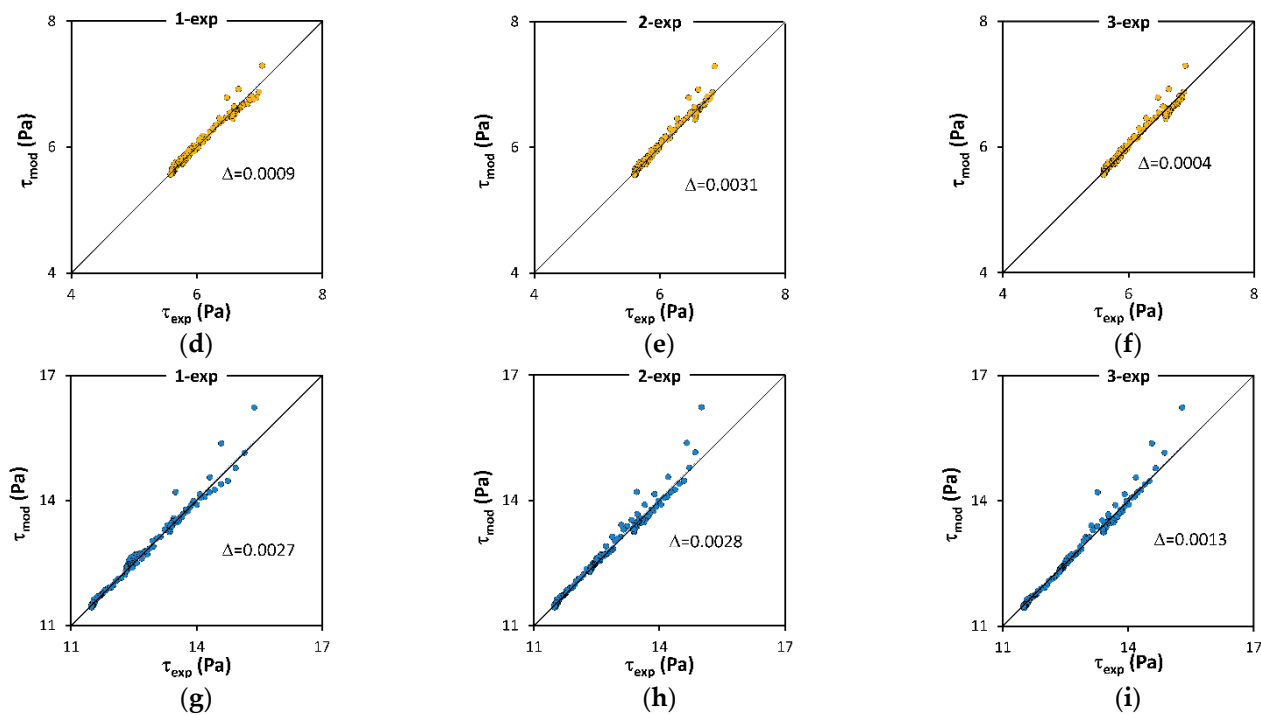


**Figure 2.** Shear stress as a function of time for different values of applied shear rate.

We observed an initial phase with decreasing shear stress values which was quite pronounced in the test carried out at maximum shear rate (i.e.,  $1000 \text{ s}^{-1}$ ); the shear stress dropped from 16 Pa to 13.5 Pa, showing a reduction of about 15.3% in the first 300 s from the beginning of the test. After that, the measured shear stress became almost stable. Such behaviour can be explained by the fact that at higher shear rates a great part of the microscopic structures were suddenly broken, therefore fewer changes in the measured behaviour occurred at subsequent instants. In any case, an analogous behaviour can be observed also at the lower shear rate (i.e.,  $100 \text{ s}^{-1}$ ) where the shear stress decreased from about 3.5 Pa to 2 Pa leading to a reduction of 43% within the same time interval. Such a behaviour was probably related to relatively complex microscopic aspects that deserve further investigation.

The three exponential models previously described (Equations (2)–(4)) have been used to describe the shear stress as a function of time for different values of applied shear rate and results were compared (Figure 3). All the exponential models provided a suitable fitting and showed the inclination to slightly overestimate the higher shear stress. In general, the calculated values of the parameter  $\Delta$  confirmed the suitability of the three models to fit experimental data, but double exponential model (Equation (3)) provided values of  $\Delta$  below 0.01 in all three testing conditions.





**Figure 3.** Comparison between experimental data and single, double, and triple-exponential models to describe the shear stress as a function of time. (a–c) are referred to  $100 \text{ s}^{-1}$ . (d–f) are referred to  $400 \text{ s}^{-1}$ . (g–i) are referred to  $1000 \text{ s}^{-1}$ .

## 4. Discussion

### 4.1. Dependence of Rheological Parameters from Non-Volatile Media

Preliminary rheological comparison of two TBS coming from two diverse high-strength wastewater treatment plants highlighted how the results are apparently not in line with previous literature findings [14]. As shown in the Supplementary Materials, TBS with higher TS concentrations but lower VS was characterized by a lower consistency index with respect to that which characterized lower concentrated sludge. Therefore, NVS influence on the rheological properties of a biological matrix has been investigated.

In this work, three types of non-volatile media were tested. Firstly, calcium carbonate ( $\text{CaCO}_3$ ) was tested as it represents a residual product of the lime reaction in water and its presence is very common in plants with chemical-physical processes (as in this specific case). Results highlight how calcium carbonate induced a relatively small effect on the rheological parameters of TBS, also increasing the concentration of NVS from  $90 \text{ kg m}^{-3}$  up to  $190 \text{ kg m}^{-3}$ . This result can be attributed to the absence of chemical interaction of  $\text{CaCO}_3$  with the water present inside the sludge. In fact, as reported by Behzadfar et al. [42], the influence of calcium carbonate on the rheological properties of fluids varies depending on particle size. They observed that higher increases in viscosity were appreciable with higher particle sizes of calcium carbonate [42]. In our study particle size was too small ( $1\text{--}3 \mu\text{m}$ ) to lead to a significant change on sludge rheological properties. Based on these results, the potential dosage before biological processes of lime composed of small-particle  $\text{CaCO}_3$  will produce circumscribed effects on the rheological parameters of TBS.

Sand was tested as NVS to understand if the rheology of BS can be affected by malfunctions of grit removal processes, which determine high quantity of granular materials entering the biological reactor. Results agree with Adeyinka et al. [43] who have explained that sand does not influence the consistency coefficient of a fluid given absence of chemical interaction between silica and water. On the contrary, Mangesana et al. [44] have highlighted how fluid viscosity can be influenced by sand dimensions, increasing with particle size. In our study, results were obtained focusing only on sand with size of  $0.16\text{--}0.24 \text{ mm}$ , therefore different outcomes with sands of diverse sizes cannot be excluded. Moreover,



an increase in consistency due to the contribution of interaction between biomass and sands over the long-term cannot be excluded, and other studies should be further developed. Probably, based on these results, the potential malfunction of grit removal processes will produce circumscribed effects on the rheological parameters of TBS, even if some experimental points in Figure 1b show a deviation from the above-described behaviour and deserve further investigation.

Sodium bentonite is a non-volatile media reducing the filtering properties of membranes [45]. For this reason, understanding the influence of this substance in membrane biological processes is a key aspect for process optimization. In this work, results highlight how sodium bentonite strongly influences rheological parameters of the investigated biological mixture, enhancing the sludge consistency coefficient about 20 times when increasing NVS concentration from 90 kg m<sup>-3</sup> to 190 kg m<sup>-3</sup>. These results agree with previous findings of Hamida et al. [46], which highlighted how even small concentrations of sodium bentonite in water produce a viscous thixotropic fluid with low filtration capacity. However, to date no results on a thermophilic biological substrate are available. This result represents a key tool for water utility operators to optimize the operating costs of the plant (e.g., pumping costs, washing of the membranes) and performance of the thermophilic biological process.

#### 4.2. Evaluation of Sludge Response after Prolonged Imposed Shear Rate

Plots of the shear stress as a function of time at a fixed shear rate were evaluated, highlighting the thixotropic behaviour of the investigated sludge sample. In particular, the obtained R<sup>2</sup> values are 0.9738, 0.9899, 0.9911, respectively for the speeds of 100 s<sup>-1</sup>, 400 s<sup>-1</sup> and 1000 s<sup>-1</sup>. These results can be related to the different speed of bond rupture in the biological matrix. In exponential models, parameters  $\alpha$ ,  $\beta$  and  $\chi$  can represent the diverse phases of rupture of the surface tension of the sludge. In two-exponential model, the parameters  $A$  and  $\alpha$  can be associated with a faster phase describing the macro-breaking of the ionic bonds and hydrogen bonds present in the sludge, while the other two  $B$  and  $\beta$  can be related with a slower phase indicating the breaking of weak bonds inside the biological structure.

The three-exponential model tried to explain the breaking of the bonds inside the sludge flake at 3 temporal moments. As can be seen from Figure 3, at the higher shear rates (i.e., 400 s<sup>-1</sup> and 1000 s<sup>-1</sup>) the three-exponential model has the lowest value of the parameter  $\Delta$  and for this reason it seems able to better mimic the 3 phases of sludge breaking.

Each exponential model was characterized by an intrinsic complexity given by the number of parameters to be fitted. The AIC index was calculated to combine the information on the accuracy that can be achieved by a model and the number of its tuning parameters (Table 2).

**Table 2.** Values of AIC index for different models in diverse shear rate conditions. (\*): best conditions.

Shear Rate (s <sup>-1</sup> )	AIC Index		
	Single Exponential	Double Exponential	Triple Exponential
100	-19.859	-39.862 *	14.883
400	-55.641 *	-41.035	-26.070
1000	102.200	89.300 *	132.827

Based on the results, for shear rate equal to 100 s<sup>-1</sup> and 1000 s<sup>-1</sup>, the double-exponential model was the best choice for describing the thixotropic behaviour (-39.862 and 89.300) while in case of 400 s<sup>-1</sup>, lower AIC was reached using single-exponential model despite the difference with double-exponential model is very limited (-55.641 vs. -41.035). Therefore, balancing accuracy and mathematical complexity of the model, double-

exponential model can be suitably adopted to describe thixotropic behaviour of TBS in this range of shear stress. The tested matrix shows a first phase in which breaking of particles bonds results in a rapid decrease of its viscosity and a second phase where the decrease of the viscosity value is slower.

## 5. Conclusions

This work aimed to quantify the influence of non-volatile media on rheological properties of TBS and to better explore the response of thermophilic sludge in case of prolonged shear rate. The results show a significant dependence of TBS from sodium bentonite concentration, while calcium carbonate and sand produced relatively lower influence. TBS response to diverse shear rates for longer period highlighted a thixotropic behaviour which is much pronounced at higher shear rate ( $1000\text{ s}^{-1}$ ). Double exponential fitting model was the best choice in terms of interpolation accuracy of the results and mathematical complexity for describing thixotropic behaviour in case of low ( $100\text{ s}^{-1}$ ; AIC:  $-39.826$ ) and high shear rate ( $1000\text{ s}^{-1}$ ; AIC:  $89.300$ ), while single-exponential model represented the best option in case of medium shear rate ( $400\text{ s}^{-1}$ ) but with limited difference with double-exponential model ( $-55.641$  vs.  $-41.035$ ).

This study represented a crucial step in gaining insight into the rheological properties of TBS, with special reference to thixotropic behaviour. Future research is needed to clarify a few aspects that have been pointed out in this work. The acquired experimental findings will be useful for managers of high-strength wastewater treatment plants, providing important information for improving the process efficiency.

**Supplementary Materials:** The following supporting information can be downloaded at: [www.mdpi.com/article/10.3390/app12105198/s1](http://www.mdpi.com/article/10.3390/app12105198/s1), Section: Dependence of rheological parameters from the thermophilic sewage sludge composition; Figure S1: Shear stress of TBS sampled from (a) plant 1 and (b) plant 2 as a function of imposed shear rate. Section: Dependence of rheological parameters from the type of NVS; Figure S2: Viscosity as a function of shear rate during TBS conditioning with (a) calcium carbonate, (b) sand, and (c) sodium bentonite. Unconditioned situation is represented by  $180\text{ g L}^{-1}$  of TS concentration.

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## Nomenclature

AIC: Akaike information criterion; BS: biological sludge; COD: chemical oxygen demand;  $\text{N-NH}_4^+$ : ammonia nitrogen;  $\text{N-NO}_2^-$ : nitrite;  $\text{N-NO}_3^-$ : nitrate; Ntot: total nitrogen; NVS: non-volatile solids; Ptot: total phosphorous; TBS: thermophilic biological sludge; TS: total solids; VS: volatile solids; 3ITT: three interval thixotropic test; WWTP: wastewater treatment plant

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