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Structural model to study the influence of thermal treatment on the thixotropic behaviour of waste activated sludge

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HIGHLIGHTS

- A thixotropic model was proposed to study the variations in the thixotropic behaviour of sludge.
- Thermal treatment reduced the viscosity and the kinetic coefficient for the breakdown.
- Thermal treatment at 100 °C reduced the CST.
- Thermal treatment improved the sludge dewatering by centrifugation.
- Thermal treatment denatured high molecular weight proteins.

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ABSTRACT

The present study proposed a thixotropic model to examine the variations in the thixotropic behaviour of waste activated sludge after the application of different thermal specific energies (E_S). The model is based on the definition of the time dependence of a structural parameter, S, which quantifies the structural level of the internal structure at any time and shear rate, and the instantaneous variations in the alignment and deformation of flocs. The thixotropic behaviour was quantified based on the kinetic coefficients for the breakdown and build-up processes, which appeared to depend on the shear rate. The application of thermal E_S significantly reduced the steady state viscosity and the kinetic coefficient for the breakdown process, suggesting that the thixotropy slightly increased. Complementarily, the sludge was further characterised to understand the variations in sludge rheology. The extracellular polymeric substances (EPSs) present in sludge were fractionated and subsequently analysed by gel permeation chromatography, which revealed that thermal treatment solubilised most of the peptides and proteins of low molecular weight but denatured the high molecular weight proteins. On the other hand, the capillary suction time increased at low thermal E_S and decreased at high thermal E_S. However, the water removed by centrifugation was increased even at low temperatures, despite the increase in the capillary suction time value.

1. Introduction

Waste activated sludge (WAS) is formed by a connected structure of biological micro-flocs, which are stabilised primarily by extracellular polymeric substances (EPSs) [1]. The floc matrix is represented by a dynamic double-layered EPS structure, in which the inner layer consists of tightly bound EPSs (TB-EPSs) and the outer layer consists of loosely bound EPSs (LB-EPSs) [2]. EPSs mainly consist of proteins, which entrap the water and actively contribute to the water-binding capacity of the sludge floc matrix [2–4]. Thereby, although a part of the water in WAS is intracellular and thus trapped within cell walls, most of the water is bound to the EPSs, which hinders the dewatering process [4,5].

A proper understanding of rheology, which is the discipline that addresses the deformation of fluids, is essential for controlling sludge treatment processes, such anaerobic digestion or dewatering [6,7]. Under normal flow conditions, WAS behaves as a non-Newtonian pseudoplastic fluid [8,9], which indicates that the viscosity decreases with the applied shear rate. This behaviour arises because the internal sludge structure changes to suit the prevailing shear rates. According to the literature, the Ostwald–de Waele model, i.e., a power-law model with no yield stress, is the most commonly used equation to represent the non-Newtonian behaviour of sludge, most likely due to its simplicity and good fitting [8,10,11]. Other models, such as the Herschel–Bulkley model [12] or the Bingham model [13], are also valid. In

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Nomenclature

a	consistency index (Pa s^n)
n	power law index (–)
k_R	kinetic coefficient for restructuration process (s^{-1})
k_D	kinetic coefficient for destruction process (s^{-1})
K	thixotropic kinetic coefficient (s^{-1})
K_{up}	thixotropic kinetic coefficient for build-up process (s^{-1})
K_{down}	thixotropic kinetic coefficient for breakdown process (s^{-1})
S	structural parameter (Pa s^{1-m})
S_0	limiting value of the structural parameter at zero shear rate (Pa s^{1-m})
S_∞	limiting value of the structural parameter at infinite shear rate (Pa s^{1-m})
S_e	steady state structural parameter(Pa s^{1-m})
S_i	initial structural parameter when a shear rate is applied, at t = 0 (Pa s^{1-m})
S'	structural parameter at time t' ($t' = t - \Delta t$) (Pa s^{1-m})
t	shear time (s)
α_{up}	kinetic parameter for build-up process ($s^{\beta_{up-1}}$)
β_{up}	kinetic parameter for build-up process (–)
α_{down}	kinetic parameter for breakdown process ($s^{\beta_{down-1}}$)
β_{down}	kinetic parameter for breakdown process (–)
$\dot{\gamma}$	shear rate (s^{-1})
m	parameter that quantifies the instantaneous alignment and deformation of sludge flocs (–)
η	viscosity (Pa s)
η_e	steady state viscosity (Pa s)
η_i	initial viscosity when a shear rate is applied (viscosity at $t = 0$) (Pa s)

contradistinction to the Ostwald–de Waele equation, these models are characterised by the presence of yield stress, below which the sample to analyse is not flowing. However, one fundamental problem with the concept of yield stress is the difficulty in determining the true yield stress [14] because its determination is not univocal and can vary over a wide range depending on the equation used.

WAS also exhibits thixotropic behaviour [15], which means that the viscosity changes over time until reaching the stationary value. There is quite a general agreement in the scientific community that thixotropy should be defined as: the continuous decrease of viscosity with time when flow is applied to a sample that has been previously at rest and the subsequent recovery of viscosity in time when the flow is discontinued [16]. A common method for measuring thixotropy is the hysteresis loop area [17], which consists of measuring the enclosed area between the up-curve and down-curve in a plot of shear stress vs. shear rate. This plot is obtained by linearly increasing and decreasing shear rate over time [17,18]. A slow breakdown kinetic process suggests that the viscosity slowly reaches the steady state value and therefore the hysteresis area becomes large. However, the hysteresis area is only a relative measure of thixotropy and does not reveal the individual kinetic behaviours of the breakdown and build-up processes [19]. Thixotropy can be better quantified using mathematical equations known as structural models. These models describe the time dependence of viscosity by means of the time dependence of a structural parameter, which is a numerical scalar measurement of the internal structure level [20]. Moreover, these models define the time evolution of the structural parameter as a function of the kinetic coefficients for the breakdown and build-up processes. Thereby, the thixotropic behaviour is determined based on the magnitude of both kinetic coefficients instead of the general parameter (hysteresis area).

The thermal treatment has been found to affect the rheological behaviour of the sludge by modifying the overall sludge properties, including structure, size of flocs and composition [21]. More specifically, thermal treatment can reduce the viscosity and hysteresis area [22] as it weakens the strength of the internal structure by disrupting the sludge flocs.

The aim of this study is to analyse the variations in the thixotropic behaviour of WAS after the application of different thermal specific energies. The rheological properties of WAS were characterised under flow conditions by measuring the steady state viscosity and thixotropy. Specifically, the thixotropy was evaluated by means of a structural model. Complementarily, the WAS was further characterised by measuring the capillary suction time (CST), soluble protein concentration and the amount of water removed by centrifugation to understand the variations in sludge rheology. Moreover, the LB-EPS and TB-EPS were extracted and subsequently analysed using gel permeation chromatography, which enabled the molecular size of proteins extracted to the bulk solution after the thermal treatment to be determined.

2. Theory

The model proposed is defined following the classical description of thixotropic structural models and allows the quantification of the thixotropic behaviour of WAS. The breakdown and build-up of the internal network with shear-time is demonstrated with an equation of state (called the constitutive equation) and two kinetic equations, which consider the time dependence of the viscosity at constant shear rate conditions. The model is based on the definition of the structural parameter, S, which quantifies the structural level of the internal structure at any time and shear rate [23]. The structural parameter is equal to zero when the internal structure is completely broken down and produces the lowest viscosity, while a complete build-up structure corresponds to $S = 1$ and yields the highest viscosity or zero shear rate viscosity. The proposed constitutive equation for a pseudoplastic fluid is:

$$\eta(S, \dot{\gamma}) = S \cdot \dot{\gamma}^{-m} \quad (1)$$

where η is the viscosity (Pa s), S is the structural parameter (Pa s^{1-m}), $\dot{\gamma}$ is the shear rate (s^{-1}) and m is a parameter that quantifies viscosity changes when a shear rate is applied (–). Eq. (1) shows that viscosity can arise not only from structural changes due to changes in the shear rate but also due to the change in the shear rate itself. The power law exponent is negative because the viscosity decreases with the shear rate for pseudoplastic fluids. After a sudden change in the share rate, the viscosity value only changes because of the shear rate effect (called start-up viscosity). This change occurs due to the instantaneous variations in the alignment and deformation of flocs and can be quantified via the m parameter. Despite this change, the structural level remains constant in size. After alignment and deformation, the structure breaks down or builds up, and the viscosity value changes following the kinetic processes that characterise the thixotropic behaviour of sludge.The time dependence of the non-equilibrium structural parameter is defined as the net breakdown and net build-up kinetic processes because of shear forces and particle interactions. Thus, the net breakdown process at a fixed shear rate depends on the