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Ultrasound, thermal and alkali treatments affect extracellular polymeric substances (EPSs) and improve waste activated sludge dewatering

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ABSTRACT

The present study investigates the effect of ultrasound, thermal and alkali treatments on the characteristics of the extracellular polymeric substances (EPSs) in activated sludge. EPSs were fractionated through centrifugation and ultrasound approaches to generate two different EPS fractions: loosely bound EPSs (LB-EPSs) and tightly bound EPSs (TB-EPSs), where the latter is the innermost fraction. An analysis of the untreated sludge revealed that the proteins, followed by the humic acids and polysaccharides, were the major constituents of the EPSs. Each of these components was primarily observed in the TB-EPS fraction. The treatments, particularly the alkali treatment, thoroughly solubilised the EPS, as indicated by the increased LB-EPS content. As a result, the viscosity of the sludge decreased, while the capillary suction time (CST) increased. The molecular weight distributions of the EPS fractions were determined through gel permeation chromatography, which revealed that the thermal treatment (80 °C) denatured the high-molecular-weight proteins. Despite increasing the CST, the three treatments improved the sludge dewatering by releasing the interstitial water trapped within the EPSs. This improvement was more important in the case of the alkali treatment, which solubilised the highest portion of EPSs and resulted in the highest reduction in the absolute value of zeta potential.

1. Introduction

Waste activated sludge (WAS) is characterised by its high water content, which hinders its handling and disposal. Accordingly, dewatering WAS is critical because it can decrease the subsequent treatment and disposal operations. The presence of extracellular polymeric substances (EPSs), which are the main component of the WAS floc matrix [1], is one of the major causes of the low dewaterability of WAS. According to Chen et al. [2] and Jin et al. [3], the presence of EPSs led to additional interstitial bound water within the WAS and poor settleability due to its large particle sizes. EPSs are primarily composed of high-molecular-weight secretions from microorganisms and the products of both cellular lysis and macromolecule hydrolysis [4]. Moreover, some of the organic matter from wastewater can also be adsorbed into the EPS matrix [5,6]. Proteins, polysaccharides and humic substances are usually the major components of EPSs [1,7]. Lipids, nucleic acids, uronic acids, and inorganic components have been found in smaller quantities [4]. The floc matrix is generally represented by a dynamic double-layered EPS structure: the inner layer consists of tightly bound EPSs (TB-EPSs), and the outer layer consists of loosely bound EPSs (LB-EPSs) [8]. The inner layer has a certain shape, and it is bound tightly and stably to the cell surface, while the outer layer does not exhibit an obvious boundary [4].

WAS dewatering can be improved through various treatments, such as ultrasound [9], alkali [10] or thermal [11] treatments. These treatments can partially disintegrate the WAS by disrupting the cell walls and solubilising the EPS, consequently releasing a portion of the interstitial water and increasing the WAS dewatering [11]. Accordingly, these treatments affect the viscosity and filterability of sludge. Rheology, which is the study of stress-strain relationships in elastic plastic and viscous materials, is a useful tool for characterising WAS [12] and is critical when designing dewatering processes [13]. Under normal flow conditions, WAS behaves as a non-Newtonian pseudo-plastic fluid [14], indicating that the viscosity decreases with the applied shear rate. The Ostwald–de Waele model is commonly used to represent the non-Newtonian behaviour of WAS [12,14]. Other models, such as the Herchel–Bulkley model or the Bingham model, are also valid. In opposition to the Ostwald–de Waele equation, these models are

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Table 1
Physical features of the waste activated sludge.

TS (g/kg)	50.8 ± 0.3
VS (g/kg)	41.4 ± 0.4
Ratio VS/TS (%)	81.5 ± 1.2
TSS (g/kg)	46.0 ± 2.3
VSS (g/kg)	39.7 ± 1.6
Ratio VSS/TSS (%)	86.4 ± 1.3
pH	6.24 ± 0.03
Conductivity (mS/cm)	5.28 ± 0.05

95% confidence intervals are shown for each value.

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 [15] because its determination is not univocal and can vary over a wide range depending on the equation used.

The aim of the present study was to analyse the effect of ultrasound, alkali and thermal treatments on the EPS matrix of WAS and provide an insight into the different mechanisms of each treatment to improve WAS dewatering. Consequently, the LB-EPS and TB-EPS fractions were characterised before and after the treatments by measuring the soluble protein, polysaccharide and humic acid contents. The viscosity and zeta potential of the EPS bulk solutions were also analysed. Moreover, gel permeation chromatography (GPC) was performed to obtain the molecular size distributions of the EPS fractions. Finally, the impact of the treatments on the viscosity and dewaterability (water removed by centrifugation and capillary suction time (CST)) of the WAS was investigated.

2. Materials and methods

2.1. WAS characteristics

The WAS samples used in this study were collected from a municipal wastewater treatment plant (WWTP) near Barcelona (Spain). After leaving the secondary tank, the sludge was thickened by the staff of the WWTP by adding a cationic polyelectrolyte (approximately 1 kg/tonne dry sludge) before centrifugation. Slight changes in the water content of the sludge could be obtained with higher doses of polyelectrolyte. The total solids (TS), volatile solids (VS), total suspended solids (TSS) and volatile suspended solids (VSS) were quantified in the laboratory by following the guidelines provided by the standard methods 2540 G [16] (Table 1). The sludge was stored at 4 °C to minimise bacterial activity until it was used.

2.2. Treatments conditions

Ultrasound, alkali and thermal treatments were conducted in this study. The ultrasonic apparatus was an ultrasonic homogeniser HD2070 (Sonopuls Bandelin) equipped with an MS 73 titanium microtip probe operating at 20 kHz. The beaker containing the sample was submerged in an ice bath to minimise any increases in the sludge temperature caused by ultrasonication. The alkali treatment was conducted at room temperature (~25 °C) by adding NaOH (Sigma–Aldrich, ref. no. 221465) (the pH of the sludge was increased to 12.3); the samples were neutralised with $HCl_{37\%}$ (Sigma–Aldrich, ref. no. 258148) (pH = 6.5–7.5) after 24 h. The reason of choosing HCl for neutralising the NaOH is because the reaction only produces water and NaCl. The NaCl concentration in sludge after neutralisation was always lower than 10 g/L. The thermal treatment was performed in a closed tank (Autoclave-Engineer, bolted-closure stirred reactor) set to 80 °C. The sludge sample (150 mL) inside the tank was heated using a heating jacket outside of the tank walls. The sample was heated to the desired temperature and maintained at that temperature for an additional 30 min. The sludge was mechanically agitated during the thermal treatment to ensure that the temperature of the sample was temporarily homogeneous. The details for each treatment are listed below; these conditions correspond to the dewatering conditions used in a previous study [17]:

- A specific energy of 27,000 kJ/kg TS (or 7.50 kWh/kg TS) was used for the ultrasound treatment.
- A NaOH concentration of 157 g NaOH/kg TS was used for the alkali treatment.
- A specific energy of 15,000 kJ/kg TS (or 4.17 kWh/kg TS) was used for the thermal treatment, which reached 80 °C.

2.3. EPS extraction protocol

The sludge stratification procedure followed in the present study was very similar to that presented by Yu et al. [18]. The protocol is described below. The WAS sample was dewatered by centrifugation at 2000 × *g* for 10 min. The supernatant was discarded, and the bottom sediments were resuspended to the original volume using a buffered solution (pH 7) consisting of Na_3PO_4 (Sigma–Aldrich, ref. no. 222003), NaH_2PO_4 (Sigma–Aldrich, ref. no. S9638), NaCl (Sigma–Aldrich, ref. no. S9888), and KCl (Sigma–Aldrich, ref. no. P3911) at a molar ratio of 2:4:9:1 [7]. The conductivity of the buffer was adjusted to match the conductivity of the WAS samples. The suspension was centrifuged at 5000 × *g* for 15 min, and the bulk solution and solid phase were collected separately. The soluble organic matter in the bulk solution was the LB-EPS fraction. The collected bottom sediments were resuspended using the aforementioned buffer solution and centrifuged again at 5000 × *g* for 15 min to eliminate the LB-EPS that impregnated these sediments. Subsequently, the collected sediments were resuspended in the buffer solution and later ultrasonicated for 10 min using an HD2070 ultrasonic homogeniser (Sonopuls Bandelin). The resulting suspensions were centrifuged at 20,000 × *g* for 20 min. The soluble organic matter in the bulk solution was the TB-EPS fraction. All of the EPS fractions were filtered through 0.45-μm low protein-binding polyvinylidene difluoride (PVDF) membranes. Therefore, once the extraction protocol was completed, 8 EPS fractions were obtained: two fractions (LB-EPS and TB-EPS) for each of the four analysed sludge samples (untreated, ultrasonicated, alkali-treated, and thermally treated). The fractionations of the untreated sludge and the three treated sludge samples were performed in triplicate.

2.4. Analysis on the EPS fractions

2.4.1. Total organic carbon, protein and polysaccharide analysis

Different parameters were measured to characterise the EPS content. The total organic carbon (TOC) of the EPS was measured with a TOC-V_{CSN} analyser (Shimadzu). The biochemical composition was studied through colorimetric methods using a Perkin Elmer UV/vis Lambda 20 spectrophotometer. The polysaccharides were quantified through an anthrone-based method (anthrone 98%, Panreac, ref. no. 162441.1606) using glucose (Panreac, ref. no. 131341.1211) as the standard [1]. The protein content was measured through the Lowry method using bovine serum albumin (BSA) (Sigma–Aldrich, ref. no. A3299) as the standard [19]. The Lowry method relies on the reaction of copper ions with peptide bonds to quantify proteins and peptides. Nevertheless, when referring to the Lowry measurement, the term protein was used for simplicity. Each of these analyses was performed in triplicate for each extraction (three extractions); the standard deviation of the nine measurements was calculated.

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