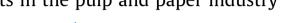
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The re-use of Waste-Activated Sludge as part of a "zero-sludge" strategy for wastewater treatments in the pulp and paper industry



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HIGHLIGHTS

• Total reuse of Waste Activated Sludge from pulp and paper industry was studied.

• The WAS hydrolysis solubilises over 90% of tCOD and hygienises the solid residue.

• It is possible to use solid residue of WAS as a raw material in cardboard production.

• Biogas can be produced from solubilised portion of WAS in an UASB reactor.

• Presented "zero-sludge" concept produces renewable energy and raw materials.

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ABSTRACT

The possibility of introducing the thermo-alkali hydrolysis of Waste-Activated Sludge (WAS) was investigated, in order to enable the use of its solid residue as a raw material in cardboard production and the use of its liquid portion for anaerobic digestion in an UASB reactor. The evaluation of the hydrolysis at pH > 12 and T = 70 °C showed that the microbe cells were disrupted with more than 90% efficiency in less than 2 h. The solid portion was hygienised, therefore making it possible to integrate it into the cardboard production as a raw material for less demanding cardboards. Up to 6% addition of the liquid portion of hydrolysed WAS to wastewater decreased the specific biogas production in a pilot-scale UASB from 0.236 to 0.212 m³/kg_{COD}, while the efficiency of the COD removal decreased from 80.4% to 76.5%. These values still guarantee an adequate treatment of the wastewater and an increased biogas production by 16%.

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1. Introduction

The residue generated during primary, secondary and tertiary wastewater treatment is often referred to as "sludge", with the sludge generated from secondary and tertiary aerobic treatments being specifically referred to as Waste-Activated Sludge (WAS). Activated sludge processes, which are the most common technologies in wastewater treatment, produce large amounts of WAS. This is composed of appreciably slowly biodegradable organic matter with a low overall biodegradability. The stability and safety of this biodegradable material prior to disposal or reuse are regulated in the European Union with increasingly strict legislation (directive on landfilling waste 1999/31/EC) (Luste et al., 2011).

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E-mail addresses: leon.kaluza@mm-karton.com (L. Kaluža), matej.sustarsic@ icp-lj.si (M. Šuštaršič), vera.rutar@icp-lj.si (V. Rutar), gregor.zupancic@ios.si (G.D. Zupančič). Biological stabilisation is considered to be one of the most attractive methods for reducing the major portion of the organic fraction in WAS, and anaerobic digestion (AD) is favoured over aerobic digestion due to the cost of aeration, the ability of anaerobic systems to maintain their temperature and the value of methane as a renewable energy resource (Whiteley et al., 2003). WAS AD can be a sustainable sludge-treatment practice, where both pollution control and energy recovery is achieved. AD prevents greenhouse gas emissions from the uncontrolled degradation of biodegradable materials in landfills and its digested bio-solids can enable the recycling of nutrients that can be used as organic fertilizers or for soil improvement. The material can also be more easily hygienised, if required (Luste et al., 2011).

One weakness of AD is the slow hydrolysis phase, and therefore the long residence time of the sludge in the anaerobic reactor, which is typically 20 days or more (Pérez-Elvira et al., 2000). The particulate organic matter contained in activated sludge is usually poorly solubilised and only 30–50% of the total chemical oxygen





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demand (tCOD) or total volatile solids (tVS) in the WAS can be biodegraded (Rajagopal and Béline, 2011). In recent years, the pre-treatment of sludge is increasingly used to accelerate the AD in many different ways, such as using thermal energy (Climent et al., 2007), acid (Neyens et al., 2003), alkali (Vlyssides and Karlis, 2004), ultrasound (Show et al., 2010), ozone (Weemaes et al., 2000), gamma rays (Yuan et al., 2008) and mechanical forces (Wett et al., 2010). In this context, the application of pre-treatment techniques for WAS has been gaining importance, with several full-scale facilities already in operation (Donoso-Bravo et al., 2011). The combination of chemical and thermal treatments was reported to be an effective approach for the reduction of WAS solids (Na et al., 2010). It was studied mostly for the hydrolysis of municipal WAS, with a smaller number of studies looking at industrial wastewater applications. However, applying thermoalkali hydrolysis revealed a noticeable increase in the solubility and biodegradability of the organics from the WAS production of juice (Vlyssides and Karlis, 2004), and the alkaline hydrolysis of WAS from paper and cardboard production substantially increased methane production during the anaerobic digestion of the WAS (Lin et al., 2009).

Based on this, the possibility of introducing a "zero-sludge" concept to the cardboard industry was investigated. Firstly, the quantity of WAS was reduced by hydrolysing and solubilising its major portion. Next, a full integration of the WAS solid and liquid fractions into an existing system of cardboard production and into the anaerobic treatment of industrial wastewater was introduced, respectively. Therefore, the following research objectives were devised:

- Optimization of the hydrolysis of the WAS, with a focus on the impact of a thermo-alkali pre-treatment.
- Hygenisation of the solid residue of the hydrolysed WAS and its reuse as a raw material in cardboard production.
- Anaerobic biodegradation of the liquid portion of the hydrolysed WAS for biogas production.

2. Methods

2.1. WAS and the conditions for hydrolysis

For the experiments, the WAS from the aerobic stage of the wastewater treatment plant (WWTP) of the cardboard producer Količevo Karton, Domžale (a member of Mayr–Melnhof Group) was used. The WWTP includes a mechanical-chemical pre-treatment that reduces the suspended solids to below 100 mg/L and the COD to below 2000 mg/L. The settled primary sludge is used as a raw material for the middle layer in the production of cardboard. The treatment is followed by a Paques anaerobic internal circulation (IC) reactor. Finally, the wastewater is treated in a conventional activated-sludge process and released into the local river. The secondary clarifier produces the dischargeable effluent as overflow and WAS (approximately 2% solids). While the primary sludge re-enters the production of the cardboard as middle-layer material, the secondary sludge remains as solid waste that is hygienically problematic. On average, 9.6 tonnes (approximately 20-25% solids) of the sludge have to be disposed daily from the WWTP.

The WAS was sampled from the secondary clarifier. The WAS had typically between 15,000 and 25,000 mg/L of total dry solids (tDS) and was hydrolysed under predetermined, optimal conditions (pH 12, 70 °C) at three concentrations: the original concentration, concentrated to approximately 30,000 mg/L by gravitational sedimentation (24 h) and thickened to approximately 40,000 mg/L by centrifugation (3500 rpm, 10 min). The thermal-alkaline hydrolysis of the sludge was performed within 24 h of

the sampling. The sludge was placed in a 2 L medium bottle into which 20% NaOH was added to adjust the pH to 12. 11 mL of NaOH for 1 L of original sludge was required to adjust its pH to 12, 8 mL of NaOH for 1 L of sedimented sludge and 7 mL of NaOH for 1 L of centrifuged sludge. The sample bottle was tightly closed to minimize the evaporation of water and volatile compounds. For a hydrolysis temperature of 70 °C, the bottle was placed on a hot, magnetically stirred plate and heated for up to 24 h as the desired temperature was reached. Longer treatment times were not considered because of the consequent increase in the energy requirements. The sample without any thermo-alkali hydrolysis treatment was referred to as the blank sample (control).

2.2. Anaerobic digestion of WAS

Pilot-scale experiments were performed to confirm the suitability of the liquid portion of the hydrolysed WAS for AD. The reactor setup (Fig. 1) was operated under equivalent conditions to the fullscale IC reactor, which has operated from 2006 in Količevo Karton WWTP. Its central part is a cylindrical vessel with a total volume of 12 L, which was inoculated with 6 L of granulated anaerobic biomass from the full-scale reactor.

The sludge hydrolysis for pilot-plant experiments were carried out with simultaneous pasteurization by injecting steam at a temperature of 100 °C into a 100 L hydrolysis reactor, mixing it within the sludge with a pH adjusted to 12 (1 L of 20% NaOH for 90 L of WAS), increasing the bulk suspension temperature to 70 °C and proceeding for 2 h. The hydrolysis reactor was equipped with valves to control the steam influent from the boiler and the sludge effluent from the reactor. At the end of the reaction time of 2 h, the effluent valve was opened and the hydrolysed sludge released to the centrifuge, where it was separated into liquid and solid portions. The sludge that was slightly diluted by the steam condensation had a pH of 10.0 at the end of hydrolysis. The liquid portion of hydrolysed WAS was not neutralized since it was planned to be mixed with a relatively low percentage (3-10 vol.%) of wastewater with a pH of 6.0–6.5. The raw wastewater and the liquid portion of the hydrolysed WAS were mixed in a 220 L influent vessel in a ratio based on the available daily quantities of WAS and the wastewater from the Količevo Karton WWTP (up to approximately 12 vol.%). The mixture was filtered through a sieve of 0.01 mm to prevent clogging of the pilot plant reactor piping. As a control substrate, only raw wastewater was used. The pH of the wastewater and the liquid portion of the hydrolysed WAS mixture increased to maximum 7.2. The influent reservoir/feeding tank was constantly mixed to ensure the homogeneity of the mixture. Based on the reactor's operating volume of 12 L, the influent was fed continuously to the reactor at a rate of 30-200 L/day using a membrane pump, for a hydraulic retention time (HRT) between 1.5 and 10 h. The temperature of the reactor was kept at 35 ± 1 °C. The reactor was also kept under the same working conditions for a period corresponding to at least 10 retention times, ensuring steadystate conditions, and maintained for at least 10 more HRTs for data collection. A H₂S trap and a humidity absorber were installed prior to the biogas measurement.

2.3. Analytical methods

The dry solids (DS) and volatile solids (VS) of the samples were determined according to standard methods, DIN EN 12880 and DIN EN 12879, respectively. The chemical oxygen demand (COD) was determined according to ISO 6060. Evaluating the hydrolysis of the waste-activated sludge, for a determination of the soluble components (sDS, sVS and sCOD), the samples were filtered of the sludge through a belt-press filter (the same as for WWTP) with a

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