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HYDROLYSIS OF SECONDARY SLUDGE FROM INDUSTRIAL WASTEWATER TREATMENT PLANT OF BOARD PRODUCTION: ENHANCEMENT OF BIOGAS PRODUCTION IN A UASB REACTOR

DISSERTATION

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Povzetek

Preučili smo možnost uporabe termično-alkalne hidrolize biološkega aerobnega aktivnega blata, da bi omogočili uporabo trdnega preostanka hidrolize kot surovine za proizvodnjo kartona in uporabo raztopljene frakcije v anaerobnem razkroju pri obstoječih obratovalnih pogojih tovarniškega UASB reaktorja. Za ovrednotenje učinkovitosti hidrolize smo spremljali naslednje parametre: delež trdnih snovi in organske komponente blata, kemijsko potrebo po kisiku (tKPK) in proizvodnjo bioplina v pilotni napravi za anaerobni razkroj. Primerjava teh parametrov pred in po termično-alkalni hidrolizi in anaerobnem razkroju je pokazala, da smo v znatni meri razkrojili mikrobne celice aktivnega blata, kar je rezultiralo v sprostitvi citoplazme in precejšnjem povečanju kemijske potrebe po kisiku v tekočem delu blata (sKPK), pri čemer je razmerje sKPK/tKPK presegalo vrednost 0.9. Termično-alkalna obdelava za hidroliziranje blata je proizvedla blato, ki ni več vsebovalo patogenih bakterij pri testiranih pogojih. Na ta način je bila omogočena možnost integracije trdnega hidroliznega preostanka v proizvodnjo kartona, saj smo dokazali, da je prišlo do popolnega uničenja patogenov v blatu. Primernost trdnega preostanka kot surovine za t.i. liner embalažo smo določili z ovrednotenjem količine, do katere dodatek hidroliziranega preostanka k standardnim surovinam vpliva na njihove optične in mehanske lastnosti. Dodatek trdnega hidroliznega preostanka k standardnim surovinam je vplival na njihove optične in mehanske lastnosti, t.j. 1 % in 5 % masni delež trdnega preostanka hidrolize je znižal utržni indeks in indeks razpoka kartonskih listov v obsegu 20-25 % in je zato uporaben v proizvodnji kartona, pri katerem ni zahtev po togosti. Poleg tega smo pokazali, da je preostala tekoča frakcija primerna za integracijo v obstoječo anaerobno čistilno napravo industrijskih odpadnih vod. Z odpravo ozkega grla anaerobnega razkroja aktivnega blata, ki ga predstavlja hidrolizna stopnja, smo z njeno termično-alkalno obdelavo v zadovoljivi meri pospešili njen anaerobni razkroj, kar smo potrdili z visoko ravnjo proizvodnje bioplina v pilotni napravi. V primerjavi z anaerobnim reaktorjem, v katerega smo dovajali samo industrijsko odpadno vodo, je akumulirana proizvodnja bioplina po dodatku hidroliziranega aktivnega blata višja za 20 %, čeprav je specifična proizvodnja bioplina po dodatku hidrolizata nekoliko nižja. Dodatek do 6 % je znižal specifično proizvodnjo bioplina iz 0.236 m^3/kg_{COD} na 0.212 m^3/kg_{COD}, medtem ko se je učinkovitost odstranjevanja KPK zmanjšala iz 80.4 % na 76.5 %. Vseeno so rezultati pokazali, da aktivno blato, ki ga termično-alkalno hidroliziramo 1 uro pri pH 12 in 70 °C, lahko integriramo v anaerobni razkroj industrijskih odpadnih vod, saj hidroliza dovolj poveča biorazgradljivost blata in skrajša zadrževalni čas, potreben za njegov anaerobni razkroj, da ostane učinkovitost odstranjevanja KPK in proizvodnja bioplina v IC reaktorju na zadovoljivem nivoju. Na ta način je naša raziskava pokazala, da je “zero-sludge” koncept obdelave biološkega aerobnega aktivnega blata v proizvodnji kartona izvedljiv.

Ključne besede: anaerobna obdelava blata, bioplin, odpadno aktivno blato, termično-alkalna hidroliza, “zero sludge” koncept

Abstract

We investigated the possibility of using the thermo-alkali hydrolysis of waste-activated sludge (WAS) to enable the use of the hydrolysis solid residue as a raw material for the production of cardboard and the use of the solubilised fraction in anaerobic digestion under the operating conditions of an industrial UASB reactor. To estimate the efficiency of hydrolysis, we compared the following parameters: percentage of total dry solids (tDS) and total volatile solids (tVS), chemical oxygen demand (tCOD) and the production of biogas in a pilot plant for anaerobic digestion. The comparison of these parameters before and after the thermo-alkali hydrolysis and the anaerobic digestion showed that we managed to disrupt it in a large proportion of the microbial cells of the WAS, which resulted in the release of the cytoplasm and in an increase of the soluble chemical oxygen demand (sCOD) in waste-activated sludge, whereas the sCOD/tCOD ratio was above 0.9. The thermo-alkali hydrolysis of waste-activated sludge produced a sludge free of pathogenic bacteria under the tested conditions. In this way, we enabled the possibility of the integration of the solid residue of the hydrolysis into the production of cardboard. We determined the suitability of the solid residue of the hydrolysed WAS as the raw material for a so-called liner packaging by evaluating the extent to which the addition of the solid residue of the hydrolysed WAS to its standard raw materials influenced their optical and mechanical properties. The solid residue of the hydrolysed WAS addition to the standard raw materials influenced their optical and mechanical properties, i.e., 1 % and 5 % solid portions of hydrolysed WAS additives decreased the tensile and burst indexes of the cardboard sheets in the range 20–25 % and can therefore be used in the production of cardboard with no demand for stiffness. In addition to this, the remaining solubilized fraction was suitable for the integration into an existing anaerobic wastewater-treatment plant. By the elimination of the bottle neck that the hydrolysis phase represents in the anaerobic treatment of WAS, the WAS anaerobic treatment was accelerated using the thermo-alkali pre-treatment. This was confirmed with the high level of biogas production in the pilot plant. In comparison to the anaerobic reactor into which we added only raw wastewater, the accumulated production of biogas after the addition of a liquid portion of hydrolysed WAS increased by 20 %, whereas the specific production of biogas was somewhat lowered. The addition of up to 6 % of the liquid portion of the hydrolysed WAS decreased the specific biogas production from 0.236 m^3/kg_{COD} to 0.212 m^3/kg_{COD}, while the efficiency of the COD removal decreased from 80.4 % to 76.5 %. Nevertheless, the results showed that the WAS that is thermo-alkali pre-treated for 1 hour at pH 12 and 70 °C can be integrated into the anaerobic digestion of industrial raw wastewater. The hydrolysis enhances the biodegradability of the WAS and reduces the detention time needed for its anaerobic digestion, while the efficiency of the COD removal and the biogas production in the UASB reactor remains at an acceptable level. Our research showed that the presented "zero-sludge" concept for the WAS treatment is feasible in the production of cardboard.

Keywords: anaerobic digestion, thermo-alkali hydrolysis, waste-activated sludge, "zero sludge" concept

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List of abreviations

BPR … biogas production rate

COD … chemical oxygen demand

DS … dry solids

HRT … hydraulic retention time

IC … internal circulation reactor

LCFA … long-chain fatty acids

LPH-WAS … liquid portion of hydrolysed WAS

sCOD … soluble chemical oxygen demand

sDS … soluble dry solids

pDS … particulate dry solids

pMS … particulate mineral solids

pVS … particulate volatile solids

sMS … soluble mineral solids

SBP … specific biogas production

SPH-WAS … solid portion of hydrolysed WAS

SRT … solids retention time

sVS … soluble volatile solids

tCOD … total chemical oxygen demand

tDS … total dry solids

tMS … total mineral solids

tVS … total volatile solids

UASB … up-flow anaerobic sludge bed reactor

VFA … volatile fatty acids

WAS … waste-activated sludge

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1. INTRODUCTION

Solid waste in the form of waste-activated sludge (WAS) from wastewater-treatment plants, both industrial and municipal, is ever harder to take care of because of new legislation constraints. Landfilling and agricultural use of the sludge are increasingly restricted due to stringent regulations concerning the tolerated composition (Appels, et al., 2008). Before final disposal, stabilization of the WAS to reduce its organic content, odour problems and pathogen contamination is necessary. As a result, the costs related to the treatment of sludge have considerably increased. The estimation is that they commonly represent 30-40 % of the capital cost and about 35–50 % of the total operating costs of the wastewater-treatment facilities (Vlyssides, et al., 2004). Therefore, drying and co-incineration of the sludge are generating interest where permits can be obtained (Appels, et al., 2008). Also of great importance is the reduction of the amount of sludge produced and the improvement of its de-waterability. The research is focused on further sludge digestion and the corresponding pre-treatment methods in order to improve the substrate solubilisation and digestibility. Increasing numbers of studies present thermal or thermo-chemical processes as a pre-treatment stage of WAS digestion (Neyens, et al., 2003; Vlyssides, et al., 2004).

The research on the anaerobic digestion of sludge started in municipal wastewater-treatment plants. A lot has been done since the enforcement of the European legislation regarding the Urban Wastewater Treatments Directive (91/271/EEC), which led to an increase in sludge production. Its main disposal routes for a long time, i.e., land application and agricultural use, have always been subject to scepticism from consumers and farmers. But also a switch to incineration as an alternative turned out to be highly debated, since it is quite expensive and needs the treatment of flue gases to remove toxic compounds. The experience from the municipal sector showed that besides legal constraints, the sludge production could present an ever larger problem to the wastewater-treatment plant operators, also because its disposal routes are subject to a growing social rejection (Bougrier, et al., 2007).

Anaerobic digestion becomes, among different disposal routes, an important way to reduce the amount of final sludge solids for disposal, because it destroys most of the pathogens present in the sludge and limits the odour problems associated with residual putrescible matter and offers the possibility to use the biogas (with approx. 60–70 vol.% of methane) into which a part of organic matter transforms to a renewable source of energy. In this way, anaerobic digestion optimises the costs of a wastewater-treatment plant and its environmental footprint. Currently, biogas is produced mostly by the digestion of the sewage-treatment sludge, with minor contributions from the fermentation or gasification of solid waste or of lignocellulosic material. It is considered an important future contributor to the energy supply of Europe, although upgrading is needed (Appels, et al., 2008).

The impact of legislation can be seen in the context of state incentives in favour of enhanced biogas production. This, together with increasing costs for external sludge disposal, has driven us to search for a more efficient treatment of sludge.

We investigated the possibility to introduce a “zero-sludge” concept into the industry for cardboard production. Firstly, we had to reduce the quantity of WAS by hydrolysing it and solubilising a large portion. Finally, we had to achieve full integration of the solid (SPH-WAS) and liquid (LPH-WAS) portions of the hydrolysis as precursors into existing system of the cardboard production and into the anaerobic treatment of raw wastewater, respectively. The first objective of our research was the optimization of the pre-treatment of the sludge. We focused on the impact of the thermo-alkali pre-treatment on disintegration and solubilisation of the WAS. Secondly, we checked the sanitation of the SPH-WAS and the possibility of recycling it back into the cardboard production. Finally, we tested the anaerobic biodegradation of its supernatant for the biogas production.

1.1. Objectives

Our main objective is to resolve the handling of the WAS in pulp-and-paper raw wastewater treatment. Currently, large quantities of this sludge are generated (3500 t annually) in our model wastewater-treatment plant of Količevo Karton. WAS is currently being disposed of in an uneconomic manner (expensive handling by waste concessionaries), which represents constraints on Količevo Karton’s operations, financial as well as energetic and environmental. In order to resolve the WAS handling in an energetically and economically sustainable manner, we will do our basic research in three phases.

Firstly, we will study the thermo-chemical hydrolysis of WAS from the pulp-and-paper industry to obtain:

- A tCOD-rich LPH-WAS that will be used in an UASB reactor to increase the production of biogas and consequently green electricity in the coupled CHP engine.
- A significantly reduced SPH-WAS that will be placed as a raw material for the production of the cardboard or for composting or other appropriate use.

Starting with the thermo-chemical hydrolysis, we will leave open the possibilities of supplementing our research with new approaches to make the hydrolysis more effective (criteria: above 60 % COD extraction of organic matter from solid to liquid phase of WAS). Based on the results of the basic research in the first phase, we will extend in the second phase our laboratory experiments with a simulation of the operation on a pilot UASB reactor in the second phase of the research. Our final objective in the third phase of the research is designing and constructing a hydrolysis reactor. We will also perform an energy and economic sustainability analysis of the whole designed process. We would like to introduce an economically sustainable, integrated system by means of energy regeneration, which would be a novelty that is possible to patent.

1.2. Hypothesis

The problem was how to make WAS from raw wastewater treatment soluble in order to use the LPH-WAS as a source of carbon in the anaerobic treatment of raw wastewater and the SPH-WAS as a raw material for the cardboard in an environmentally and economically sustainable way. We are starting from the following hypotheses:

1) Our first hypothesis is that it is possible to achieve with the help of the thermo-chemical hydrolysis of the WAS at least a 60-%-dissolution of TCOD which results in high enough percentage of organic matter in LPH-WAS and low enough percentage of organic matter in SPH-WAS.
2) Our second hypothesis is that the SPH-WAS is suitable as the raw material for the cardboard production.

3) Our third hypothesis is that the LPH-WAS can be anaerobically digested in the UASB reactor.
4) Our forth hypothesis is that it is possible to integrate the hydrolysis reactor together with the heat regeneration system into the existing system of the cardboard production.

We will develop a new way of converting the WAS from pulp-and-paper raw wastewater treatment to a raw material and renewable energy. New procedures for sludge hydrolysis will be established and will enable us to construct an effective hydrolysis reactor that will be integrated into an existing system for the anaerobic treatment of pulp-and-paper raw wastewater. At the present time no such solutions are available, but in the near future new legislative constraints will require such, or similar, sludge handling. This research will present an innovative approach to solve the current problem of WAS use and disposal.

1.2.1. Research goals

WAS samples from the secondary-sedimentation tank of the pulp-and-paper industrial wastewater-treatment plant of Količevo Karton, Domžale will be obtained. The plant uses a combined anaerobic-aerobic treatment, an UASB reactor followed by a conventional WAS process, which produces 3500 t of WAS annually, dewatered to 20 % DS. This WAS will be used in the hydrolysis experiments in the first phase of our research, where the optimal conditions of the hydrolysis will be determined using sodium hydroxide or hydrochloric acid.

- For anaerobic digestion in the second phase of the research, the pilot UASB reactor will be inoculated with the biomass from the UASB reactor of Količevo Karton. The UASB will be fed with the mixture of LPH-WAS and raw wastewater from Količevo Karton.
- Based on the results of the first two phases and the available quantity of WAS (3500 t annually), a large-scale hydrolysis reactor will be designed and constructed. In the reactor design, we will consider the optimal hydrolysis parameters to define its volume (volumes up to 100 m^3 are expected) and

hydraulic retention time (1-24 hours are expected) together with the parameters of its energy balance to define its materials and its dimensions.

- In this way, the methane yields for different organic loading rates of the UASB will be determined, as well as whether its capacity can be fully reached with the addition of the LPH-WAS. For cases of not reaching full capacity and for cases of irregular situations with a smaller amount of raw wastewater, the mixtures with higher quantities of the LPH-WAS in the raw wastewater will be tested.
- An adaptation to the existing biological system with an integrated hydrolysis reactor will be proposed (Figure 1), which will operate with a heating loop based on the regeneration of energy and minimal parasitic energy demand.
- To simulate the integration of the SPH-WAS into the cardboard production, admixtures of different raw materials for the cardboard production (waste paper and fresh fibres) and SPH-WAS will be prepared. Cardboard sheets will be formed from these admixtures and their optical and mechanical properties compared with those of the sheets without the addition of SPH-WAS in order to determine the suitability of SPH-WAS for use as a raw material.

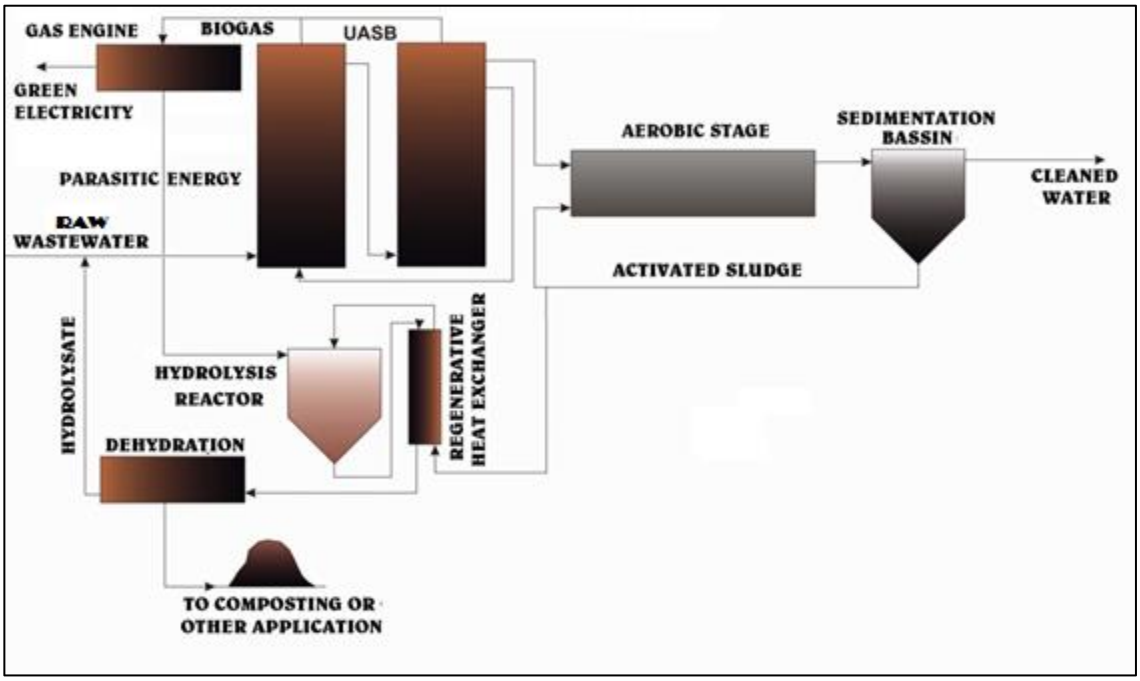


Figure 1. Presented concept of WAS treatment.

2. THEORETICAL PART

2.1. Anaerobic digestion of raw wastewater and sludge

For decades, aerobic and anaerobic treatments have been used to remove the biodegradable organic pollutants present in the wastewater generated during various industrial processes (Chinnaraj, et al., 2006). Anaerobic treatment technology has developed remarkably during the past two decades for the treatment of specific industrial wastewaters, mainly consisting of soluble and easily degradable organic substances in high concentrations. This success in the developments of anaerobic wastewater technology can be attributed to the introduction of innovative bioreactors, i.e., the anaerobic fixed bed, the anaerobic fluidized bed, and the upflow anaerobic sludge bed reactor (UASB) (Uemura, et al., 2000). Recently, the UASB process in particular is being adopted in many industries to treat the wastewater that has relatively high levels of organic pollutants due to its enhanced performance and cost-saving advantage. The UASB quickly represented more than 50 % of the installations in operation, i.e., around 850 out of 1600 units around the world. It has been applied successfully to treat wastewater from the vegetable-processing, distillery, petrochemical, pulp-and-paper industries, etc. (Chinnaraj, et al., 2006). In the pulp-and-paper industry the anaerobic process has been successfully applied in the treatment of nontoxic and easily biodegradable wastewaters, such as the effluents from mechanical pulping, paper recycling and evaporator condensates (Buzzini, et al., 2007). When economic concerns and the rate of treatment are considered, the anaerobic treatment offers a viable treatment option for pulp-and-paper wastewaters in comparison to other typical treatment processes for pulp-and-paper effluents like chemical precipitation, lagooning and activated sludge. It is perfectly suited to effluent from the pulp-and-paper industry, which typically has a low biodegradability. This is indicated by its high COD/BOD ratios, often in the range of 4–6, high lignin content, high absorbable organic halide (AOX) concentration (due to the bleaching process), colour and potential toxicity components (Tezel, et al., 2001).

When the anaerobic digestion of sludge is concerned, it can be concluded that even though current anaerobic technology seems to have reached maturity in the treatment of industrial wastewater (Uemura, et al., 2000), its application to matter that contains high concentrations of particulate organics and inhibitory organic and inorganic substances, still represents a challenge. Conventional digesters employed to process thermally hydrolysed sewage sludge were continuous-flow stirred tank reactors (CSTR). These were designed and operated so that the solids and liquids travelled through the reactor together with the same retention time, i.e., the solids retention time (SRT) equalled the hydraulic retention time (HRT). This resulted in a normal HRT period that was as long as 20 days. Later high-rate anaerobic treatment systems were introduced, characterized by a high ratio of SRT over HRT, which have become popular because of the shorter HRT, the smaller reactor volume, and the lower construction costs. However, these high-rate systems have been operated mostly for the treatment of wastes with a low solids content, for example, suspended solids below 8000 mg/L in the UASB reactor. Better for this purpose than the UASB are recent developments such as the anaerobic sequencing batch reactor (ASBR), which have made it possible to treat high-solids waste streams with a high-rate system (Wang, et al., 2009).

As mentioned, the potential of the anaerobic digestion of sludge attracts ever more interest since it reduces the problems with organic waste disposal through the reduction of the quantity of sludge by at least 30 % and through the destruction of pathogenic organisms, and is at the same time coupled with the production of biogas as a renewable source of energy (Bougrier, et al., 2007). For these reasons, anaerobic sludge digestion optimises the costs and can be considered as a major and essential part of any modern wastewater-treatment plant. Nevertheless, despite these advantages, one cannot overlook some of the limitations that can be summarized from the studies as follows: 1) only a partial decomposition of the organic fraction, 2) a rather slow reaction rate and the associated large volumes and high costs of digesters, 3) vulnerability of the process to various inhibitors, 4) a rather poor supernatant quality produced, 5) the presence of other biogas constituents such as carbon dioxide (CO_2), hydrogen sulphide (H_2S) and excess moisture, 6) the possible presence of volatile siloxanes in the biogas that can cause serious damage in the energy users (CHP, boiler) due to the formation of microcrystalline silica, and 7) the increased concentration of heavy metals and various industrial organics in the residual sludge due to the significant reduction of the organic fraction during digestion, leaving the mineral and non-degradable fraction untouched (Appels, et al., 2008).

In pulp-and-paper sludge, essentially all the organic material can be digested, except for stable woody materials, since anaerobic micro-organisms poorly degrade lignin. Besides that, the anaerobic digestion of degradable biosolids is also limited by long detention times (20–30 days) and a low overall degradation efficiency of organic dry solids (30–50 %). The reason for this is the slow hydrolysis step, during which the cell walls are ruptured and extracellular polymeric substances are degraded into the organic material available for the acidogenic microorganisms. This is particularly important in the digestion of sludge, since the major constituent of its organic fraction are cells, being relatively difficult substrates for microbial degradation (Yunqin, et al., 2009).

According to the studies, the time for an effective anaerobic digestion presents a major challenge for any system where care has to be taken for a significant amount of sludge. Sludge hydrolysis is considered as the rate-limiting step, which can only be overcome with an appropriate sludge pre-treatment.

2.1.1. Anaerobic digestion of pulp-and-paper sludge

It is not only in the pulp-and-paper industry where it can be seen that while anaerobic digestion is commonly practiced in the municipal sector, it has not gained much popularity in the industry overall. In the pulp-and-paper sector there is no full-scale anaerobic digestion facility for the digestion of solid residues (Yunqin, et al., 2009). Since the late 1980s and early 1990s, several investigations were conducted to explore the use of anaerobic digestion for treating pulp-and-paper solid residues. The studies were performed on both laboratory and pilot-scale systems. Although the results of these studies generally showed that the anaerobic digestion of pulp-and-paper biosolids could reduce the amount of solid waste by 30–70 %, with the benefit of methane production, due to the large amount of slowly digestible organics (e.g., lignin) in pulp-and-paper sludge and its long sludge-detention times, high operating costs appeared to be the reason for the lack of subsequent mill installations. Recent technological advances that reduced the detention-time requirement have been the development and establishment of sludge pre-treatment. Since the feasibilities of most of the pre-treatment technologies have been demonstrated using municipal activated sludge, the same needs to be proven on the pulp-and-paper sludge. This with its specific composition – protein (22–52 %), lignin (20–58 %), carbohydrate (0–23 %), lipid (2–10 %) and cellulose (2–8 %) fractions – but a higher volatile fraction compared to the municipal activated sludge could still turn out to be sufficiently appropriate for pre-treatment technologies. The biological treatment of pulp-and-paper sludge should gradually become the main route, rather than land filling and incineration.

2.2. Hydrolysis of WAS

The cell envelope of microorganisms in WAS is a semi-rigid structure that provides sufficient intrinsic strength to protect the cell from osmotic lysis. Microbial cell walls contain glycan strands that are cross-linked by peptide chains which cause a resistance to biodegradation (Yunqin, et al., 2009). Here, the successful application of an advanced anaerobic digestion process requires the efficient channelling of carbon from complex particulate substrates to methane gas. During the hydrolysis, the cell´s lipids degrade to long-chain fatty acids (LCFA) and volatile fatty acids (VFA) and the protein hydrolyses to ammonia and VFA (Wilson, et al., 2009). For this to occur, a pre-treatment disintegrates the flock structure of the sludge and extracts both intracellular and extracellular materials before the sludge is sent to the digester (Yunqin, et al., 2009). Using, for example, thermal or thermo-chemical hydrolysis, the sludge cells are destroyed by applying high temperature, optionally together with high pressure (Wett, et al., 2010). The organic compounds are solubilised, especially the refractory compounds, and so are consequently made more biodegradable. A linear relation between the solubilisation and the biodegradation has been found. The breakdown of the gel structure of the sludge during the thermal pre-treatment releases the intracellular bound water. The resulting reduction of hardly degradable materials improves the overall removal efficiency of the organics in the digestion process and lowers the content of volatile solids (VS) in the digested sludge (Wett, et al., 2010). Besides a high level of solubilisation and biodegradation, which accounts for the improvement in the biogas production, a modification of the sludge characteristics, and the increase in its filterability and the viscosity reduction, better dewatering, and stabilization of the sludge through the reduction of pathogen micro-organisms is achieved. The time of digestion and the final quantity of the residual sludge can thus be reduced (Bougrier, et al., 2007).

Along with the advantages, the drawbacks of hydrolysis have to be considered. Since wastewater sludge contains significant fractions of both lipid and protein, it is reasonable to surmise that compounds that are inhibitory to methanogenesis, such as ammonia and hydrophobic fatty acids, could arise through the thermal hydrolysis of proteins and lipids. It is, however, unclear which intermediates may be produced in sufficient quantities to impose a meaningful disruption or inhibition on the methanisation process (Wilson, et al., 2009).

2.2.1. Factors effecting sludge hydrolysis

When we consider a thermal or thermo-chemical treatment, its influence on the sludge characteristics (COD-solubilisation, dewaterability, percentage of particulate dry solids (pDS) in the filter cake etc.) has been studied intensively during the past decade and the research is dealing mostly with the influence of the following parameters on the process: temperature, pH and reaction time. Hydrolysis temperature, more so than contact time, seems to govern the extent to which sludge disintegration occurs. Studies divided the thermal pre-treatment to the moderate temperature range of 60–100 °C, the medium temperature range of 100–175 °C and the high temperature range of 175–225 °C (Vlyssides, et al., 2004). For specific temperatures, the solubilisation of aggregate constituents of sludge samples (e.g., lipids, polysaccharides, proteins, COD, etc.) has been reported, including its effect on the biological methane potential. The optimal temperature is, according to several authors, approximately 160–200 °C. A thermal treatment in this range, combined with anaerobic digestion, can strongly reduce sludge production – this reduction can reach as much as 50–70 % – and increase the methane yield. At higher temperatures the biodegradability of sludge is no longer improved, and it is also possible for a sharp reduction to occur. This was explained with the formation of refractory compounds linked to the Maillard reaction (Bougrier, et al., 2007), or recalcitrant soluble organics or toxic/ inhibitory intermediates (Wilson, et al., 2009).

Besides such findings from the enhancement studies of the anaerobic digestion of sewage sludge by thermal treatments, studies concerning the pre-treatment of some other solid waste types also confirmed the increase of conversion into biogas, e.g., the thermal hydrolysis of manure, which was also found to be most effective close to the optimal temperature range for the thermal hydrolysis of sewage sludge (Carrère, et al., 2010).

At lower temperatures, combined with alkaline or acidic conditions, the thermo-chemical pre-treatment was applied. A treatment in the alkaline range showed that sludge solubilisation can be significantly increased (Vlyssides, et al., 2004; Chen, et al., 2007)

2.2.2. Thermo-alkali hydrolysis of WAS

In wastewater-treatment plants, anaerobic digestion can be applied to primary (solid residue from mechanical pre-treatment) and secondary biological (WAS) sludge. However, WAS is known to be more difficult to digest than primary sludge. With respect to its degradation, the hydrolysis of its particulate organic matter to soluble substances was ascertained to be the rate-limiting step. It was reported that only 30–50 % of the tCOD or VS in WAS was biodegraded in 30 days if the particulate organic matter contained in the WAS was not properly solubilised (Chen, et al., 2007). In order to improve the hydrolysis, an anaerobic digestion pre-treatment can be used (Bougrier, et al., 2007). The need for the sludge disintegration led to pre-treatment technologies being developed for both accelerated hydrolysis rates and the advanced bioavailability of solids for the subsequent digestion process. Several methods have been studied, including thermal (neutral, acid, alkaline), (thermo-) chemical (oxidation: H_2O_2, O_3, O_2...), ultrasonic (cavitation), mechanical (high-pressure homogenization) and (micro) biological (Yunqin, et al., 2009). Of these, the thermal hydrolytic pre-treatment (THP) can be targeted at both primary sludge and WAS. Because THP holds the combined benefits of decreasing the quantity of biosolids and increasing its biodegradability, it is of greater interest to the wastewater industry (Wilson, et al., 2009). Considering the economic aspects, on the other hand, the thermal pretreatment of sludge consumes, for an increase in biodegradability, a substantial amount of energy in comparison to, e.g., chemical hydrolysis. To enhance the dewaterability of the sewage sludge, the potential of acid hydrolysis has been confirmed. For enhancing the biodegradation of complex waste, such as lignocellulosic materials, studies have suggested an alkali pre-treatment as the best method (Yunqin, et al., 2009).

From the practical point of view, the benefits of pre-treatment also include reduced requirements in terms of residence (detention) time and reactor volume as well as an enhanced biogas production. The overall improvement in the sludge-stabilization performance also reduces the final VS concentration and viscosity for increased dewaterability and represents a substantial cost saving for biosolids disposal (Wett, et al., 2010).

2.3. WAS at Količevo Karton

From the perspective of our scientific problem, the studies come down to the following common points of interest. How to overcome the limited anaerobic digestion of WAS as a solid substrate, which itself is not easily biodegradable? How to realize, withinn an acceptable time and economic frame, an effective hydrolysis as the limiting step of the anaerobic digestion of WAS? How to, based on the mechanism of the WAS hydrolysis, select appropriate experimental parameters to achieve the above goal? And finally, how to apply laboratory-scale experiments to an industrial UASB for pulp-and-paper raw wastewater and WAS?

These issues are next summarized in more detail from the studies presented.

2.3.1. Cardboard production in Količevo Karton

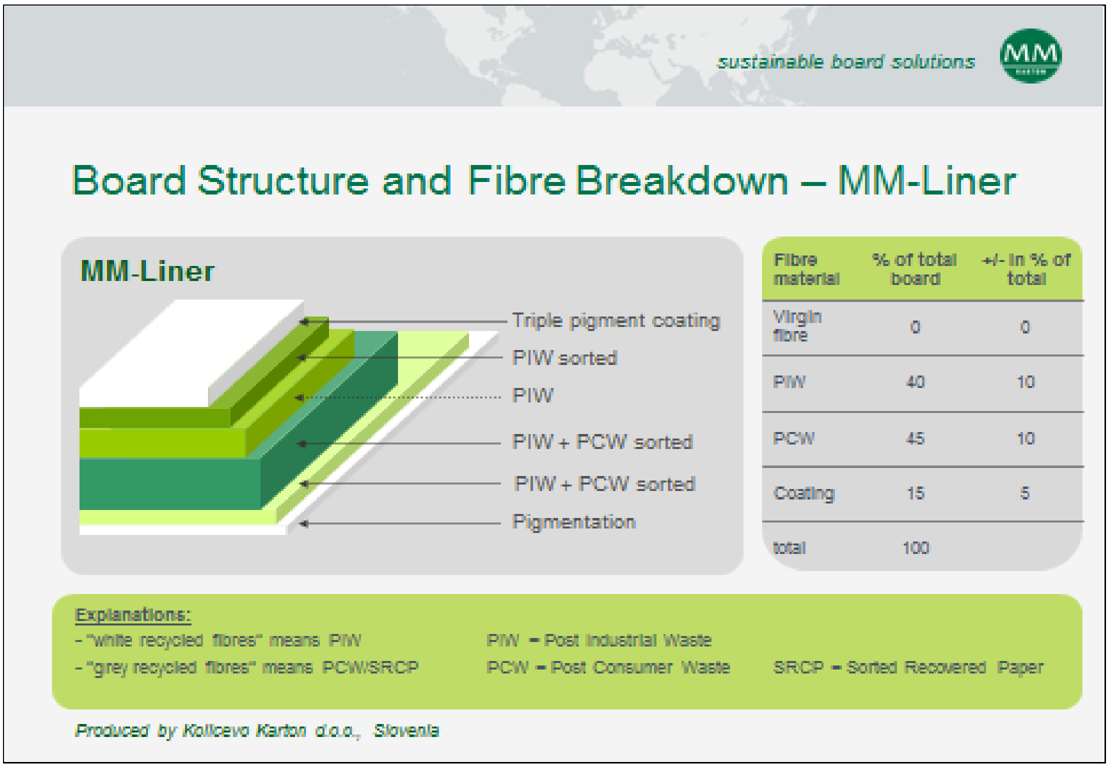
The cardboard industry is part of the paper industry, which produces mainly millboard (but no corrugated board) from a grammage starting from 180 gsm for packaging. Compared to paper in terms of structure, paper has one layer, whereas cardboard has several. Furthermore, paper and cardboard are divided into different categories on the basis of their grammage range and structure. Material with a weight of 180 gsm and above is classified as cardboard.

Around 35 million tons of cardboard are produced world-wide (excluding liquid packaging board). In Europe, 7 million tonnes of folding cardboard are produced annually for various packaging applications in the food and non-food sectors. In Europe, some 2.6 million tons of cardboard are produced from primary fibre and around

3.6 million tons are produced from secondary fibre per year. Količevo Karton, Domžale, is a part of Mayr-Melnhof Karton, Vienna, which is the world‘s largest producer of coated cardboard made from recovered fibres, as well as holding an increasingly strong position in the production of virgin-fibre-based cardboard. In seven European mills on nine board machines with an annual capacity of more than 1.6 million tonnes, it produces a wide range of folding boxboard and white-lined chipboard qualities as well as offset and flexo liner.

Recycled cardboard is cardboard containing recycled fibre. There is no standard figure for the percentage of recycled fibre that has to be used in the production of recycled cardboard. Cellulose fibres can be recycled 5 to 7 times, until the fibre length shortens to a point where their characteristics no longer fulfil their technical function. For that reason, primary fibres have to be added for the production of cardboard. Secondary or recycled fibres are cellulose fibres that come from waste paper that is collected for recycling from the paper industry, retail outlets and the domestic waste chain. Recycled fibres are divided into "pre-consumer waste" and "post-consumer waste", depending on whether the collection took place before or after use by the consumer. In the manufacture of cardboard made from secondary fibre, high-quality waste paper and waste cardboard are used. This is a substantial contribution to improved waste-paper disposal. Cardboard made from secondary fibre can also be a cost-effective alternative to fresh-fibre grades. Thanks to improved methods of fibre selection and cleaning, cardboard made from recycled fibre meets the packaging requirements in nearly all areas of the food industry. The paper-and-cardboard industry has so far identified over 50 different qualities of waste paper.

Količevo karton, Domžale, uses approximately 80 % of fibres from the waste paper of different quality classes for the production of coated cardboard grades. White waste paper is suitable for the top and back layers and mixed waste paper for the middle layer. Waste paper is added to the pulper, where it is disintegrated into the suspension of fibres. The suspension is filtered through holes with a diameter of 2.6 mm and then on a 0.25-mm sieve. The paper suspension is collected in the machine chest. The pulp is pumped on the machine sieves where the top, middle and back layers are formed. The layers are adhered to each other with the help of starch. The cardboard belt is dried with the help of steam in the press section. Finally, the cardboard is coated with calcium carbonate on both sides. The result is a multilayer cardboard that is suitable for the packaging of pharmaceuticals, food, tools, etc. A special cardboard grade called liner board is applied as a coating for the corrugated composite (Figure 2).



sustainable board solutions

Board Structure and Fibre Breakdown – MM-Liner

MM-Liner

Triple pigment coating
PIW sorted
PIW
PIW + PCW sorted
PIW + PCW sorted
Pigmentation

Fibre material	% of total board	+/- in % of total
Virgin fibre	0	0
PIW	40	10
PCW	45	10
Coating	15	5
total	100	

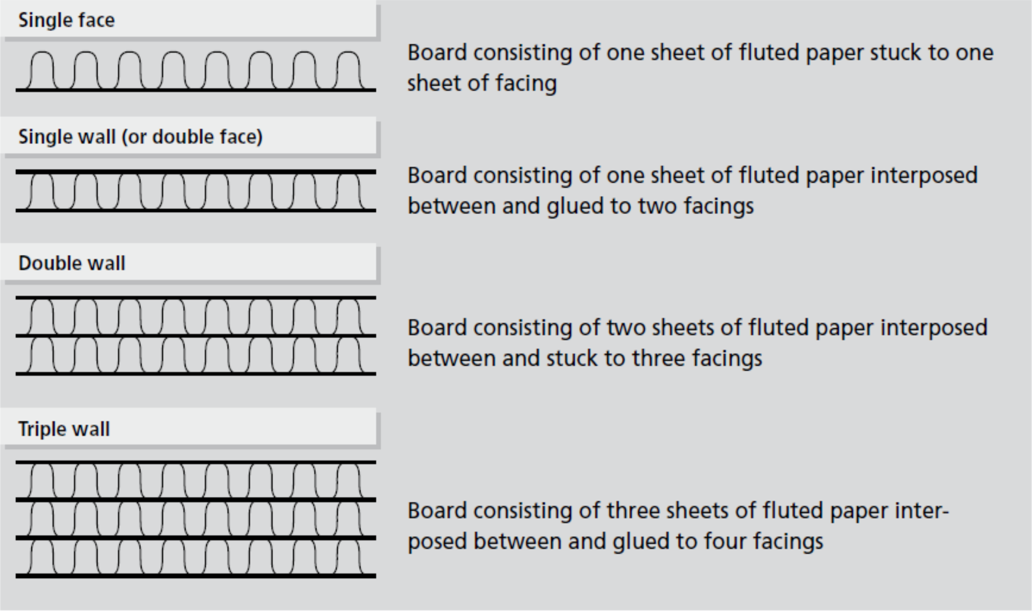
Explanations:
- "white recycled fibres" means PIW
- "grey recycled fibres" means PCW/SRCP

PIW – Post Industrial Waste
PCW – Post Consumer Waste
SRCP – Sorted Recovered Paper

Produced by Kolicevo Karton d.o.o., Slovenia

Figure 2. Technical specification of the liner board grade.

A white top testliner is a white testliner coated with a coating colour containing pigments. The corrugated board is manufactured from a number of specially conditioned layers of recycled and/or virgin papers, called fluting medium and liner board (Figure 3).



Board consisting of one sheet of fluted paper stuck to one sheet of facing

Board consisting of one sheet of fluted paper interposed between and glued to two facings

Board consisting of two sheets of fluted paper interposed between and stuck to three facings

Board consisting of three sheets of fluted paper interposed between and glued to four facings

Figure 3. Various structures of corrugated fibreboard acc. to ISO 4046.

Optical properties are essential for a white top testliner. As a consequence, the surface of a white top testliner needs to meet certain criteria in term of brightness, roughness and sizing conditions. Less important are its strength properties, since these are provided by the fluted core of the corrugated composite.

2.3.2. Wastewater-treatment plant in Količevo Karton

In 2006 Količevo Karton installed an anaerobic pre-stage to the existing aerobic water treatment plant to make the cleaning of the industrial wastewater more efficient. An IC reactor (Biopaq® Internal Circulation reactor, 21-m-high tower with a diameter of 7.3 m and the hydraulic retention time of 4 hours) was installed to convert dissolved and degraded organic impurities from wastewater to biogas (Figure 4).

Figure 4. IC reactor in Količevo Karton.

After being mechanically pre-cleaned on two sedimentators and one flotator, the wastewater (290 m^3/h, tCOD 1000-2500 mg/l, 10 meq/l VFA, 100 mg/l suspended solids) from our two cardboard machines (KS2 and KS3) comes to the anaerobic stage (Figure 5). Here the major part of organic impurities is degraded (80 % of tCOD). Before the wastewater enters the IC reactor, it is collected in a reception basin (1000 m^3), which at the same time is also an equalization reservoir for the neutralization of incoming flow peaks. From here, it is evenly pumped into the buffer basin (1000 m^3), where it is mixed with nutrients in the form of phosphoric acid and urea. This mixture enters the IC reactor through a control loop for the temperature and pH, which blocks the entrance to the IC reactor if two vital parameters do not fulfil the conditions: the temperature is regulated to an optimal 35±2 °C inside the counter-flow liquid-liquid heat exchanger (heated water from the cooling loop is used later on the cardboard machine), while the pH is corrected with sodium hydroxide when it decreases below 6.5.

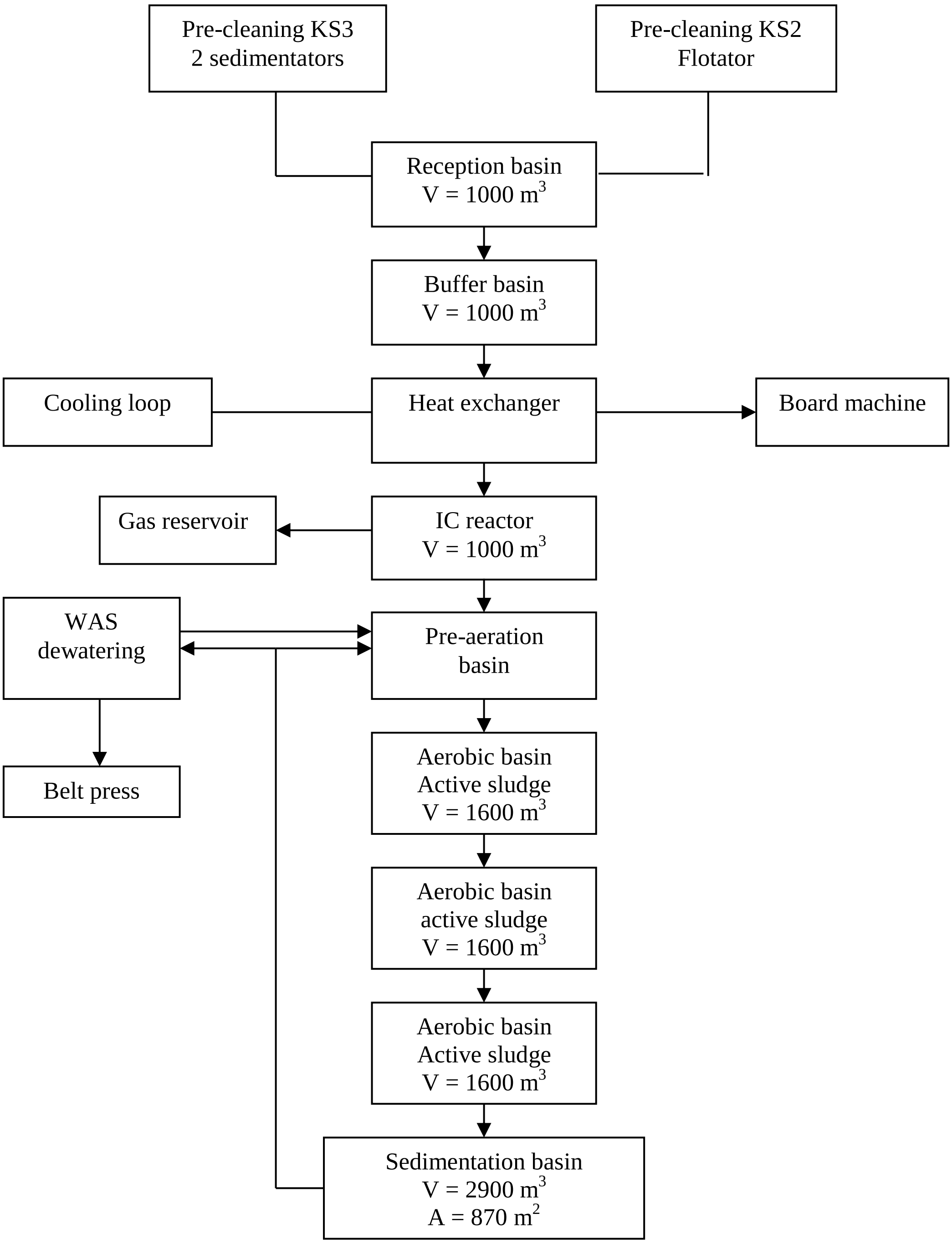


Figure 5. Combined anaerobic–aerobic wastewater treatment.

The IC reactor consists in principle of two UASB reactor units (Figure 6) that are positioned one above the other. Within the lower one, highly loaded wastewater degrades and the upper one serves to complete the degradation and to separate the liquid and gaseous phases. The rise of the wastewater from the lower to the upper part of the

IC reactor is driven by the biogas produced inside the lower part, which rises together with the wastewater because of its buoyancy.

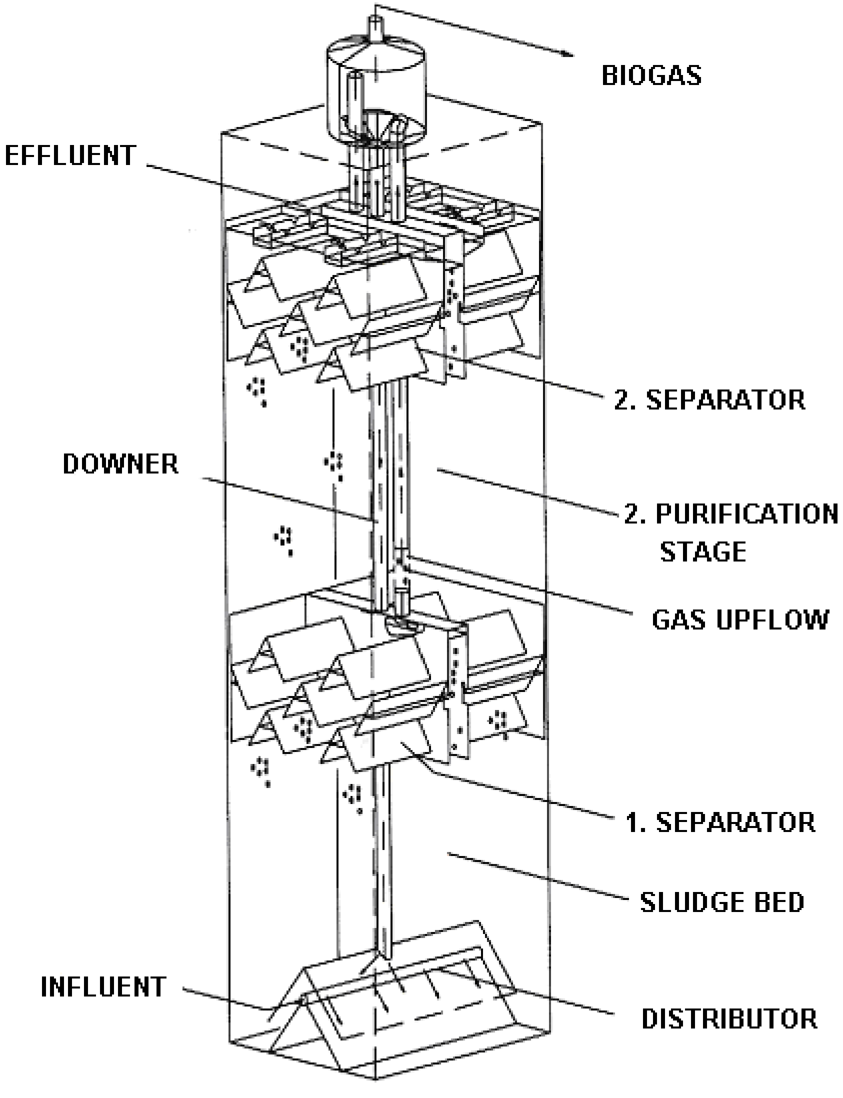


Figure 6. IC reactor.

The biggest advantage of internal circulation of the waste mixture is that the maximum contact is established between the sludge and the raw wastewater, already at the entrance and throughout the height of the reactor. Raw wastewater enters the reactor at its base, where it is immediately mixed with the existing mixture of raw wastewater and biomass, i.e., with the back-flow from the top of the reactor. Inside the lower part of the reactor sludge bed, the main part of COD is degraded and the produced biogas causes an increase in the mass (0.2-0.3 m^3 of biogas per 1 kg of COD degraded). The biogas at the reactor´s top separates from the biomass-wastewater mixture and leaves the reactor (up to 200 m^3/h, 80-90 vol.% of methane, 1,000,000 m^3 annually) to the gas tank (90 m^3). Then it is transported through a bio-filter for desulphurization to a gas CHP diesel motor (nominal power 520 kW) where the electricity is generated (340 kW of average power, 74 €/MWh as a premium for the electricity from a renewable source).

Partially treated water leaves the IC reactor at its top and continues its way to the first of the three aerobic basins (1600 m^3). The remaining biomass-wastewater mixture returns through the so-called “downer” to the bottom part of reactor where it continues, together with the newly entered raw wastewater, the process of internal circulation. After the aerobic cascade, the wastewater sludge is separated from the wastewater in a sedimentation basin (2900 m^3). Part of the wastewater sludge is recycled as so-called “activated sludge” through a pre-aeration basin, while the WAS is transported to a belt press where it is dewatered and thickened to 20 % DS. This represents solid waste (3500 t annually), the disposal of which is a cost for the factory (to the local landfill in previous years, presently to an incineration plant in Austria; cost approx. 100 €/t).

Again, this expense, together with the mentioned biogas incentive, are the reasons why we want to hydrolyse WAS and use it as a co-substrate for our IC reactor to enhance its biogas production.

3. MATERIALS AND METHODS

3.1. Hydrolysis of WAS

Our interest in the first phase of the research was to make the solid waste of a biological wastewater treatment plant soluble in order to use it as a source of carbon for anaerobic bacteria in an environmentally and economically sustainable way. We faced this challenge in our experimental approach using thermo-chemical hydrolysis, which is presented in this section.

3.1.1. Experimental conditions

The WAS samples were taken from the secondary-sedimentation tank of the pulp-and-paper industrial wastewater-treatment plant of Količevo Karton, Domžale (Figure 7). The plant uses a combined anaerobic-aerobic treatment, an UASB reactor followed by a conventional waste-activated process. The WAS is usually dewatered to 20 % dry solids (DS), with the samples for our research being taken before the belt press (WAS concentration approx. 15 g/kg DS). For the purpose of the first phase, we analysed the WAS as is, and then the WAS was also compared after it was concentrated to approx. 25 and 30 g/kg DS by settling at 4 °C for 24 hours and by centrifugation, respectively.

Figure 7. Wastewater-treatment plant in Količevo Karton with the secondary-sedimentation tank in the front.

- We collected WAS every day prior to each experiment and kept it in cold storage (4 °C). We analysed it for tCOD, sCOD, DS, VS and pH according to the standard methods for the examination of water and wastewater (ISO6060) (DIN12879) (DIN12880).
- We performed the thermo-chemical hydrolysis of WAS using a combination of heating and the addition of acid or alkali. In order to study the hydrolysis process, we performed a series of experiments under various temperatures and pH conditions. A combination of experimental sets was carried out at 25, 70, 95, 140-200 °C (in steps of 20 °C) at pH 2 and 12. The pH was adjusted by pre-mixing the WAS with sodium hydroxide or hydrochloric acid. We also produced a series of blank samples, firstly where the pH was not adjusted and secondly where no thermal treatment was applied at the pH of 2 or 12. Other samples were mixed with appropriate quantities of industrial-grade chemicals, 20% NaOH or 30% HCl (both TKI Hrastnik; 20% sodium hydroxide solution was prepared from 50% industrial-grade sodium hydroxide, of which 40 ml were mixed into 60 ml of tap water) to achieve defined pH levels and treated at all temperatures. The pH which was set at the beginning was measured at different times when the sampling was carried out. To increase the pH of 2000 ml of WAS up to 12.0, 22 ml of 20% NaOH was added. To decrease the pH of 2000 ml of WAS to 2.0, 24 ml of hydrochloric acid was added.

3.1.2. Experimental setup

The first-phase protocol of the experimental work was as follows:

- For the hydrolysis at temperatures below 100 °C, we heated the WAS in a closed glass beaker on a magnetic stirrer. The beaker with a working volume of 2000 ml was maintained at room temperature (27+/–3 °C) and at 70 and 95 °C. The beaker was magnetically stirred at 400 rpm. The batch hydrolysis processing below 100 °C was monitored in starting intervals of one hour to obtain intermediate results and took altogether up to 24 hours to establish the stationary phase, where the maximum COD extraction to the liquid phase is expected.

- For the hydrolysis at temperatures from 140 to 200 °C a 200-ml reactor was constructed as a pressure vessel with a heating shell and equipped with a pressure-relief valve. The temperature of the WAS–acid or WAS-alkali mix was kept constant by setting the temperature of the outer heating shell of the reactor. The temperatures in the reactor were kept constant to within ±2 °C of the set-point. Figure 8 illustrates the experimental set-up. Samples of 200 ml of WAS were batch-treated under different, but fixed, operating conditions. They were compared to the samples without either an acid or alkali thermal-hydrolysis treatment, which were referred to as 'blank' samples. The batch-reactor hydrolysis process took up to 2 h, and by terminating it a sample for the analysis was taken and divided into two portions for the analysis of the total and soluble parameters.

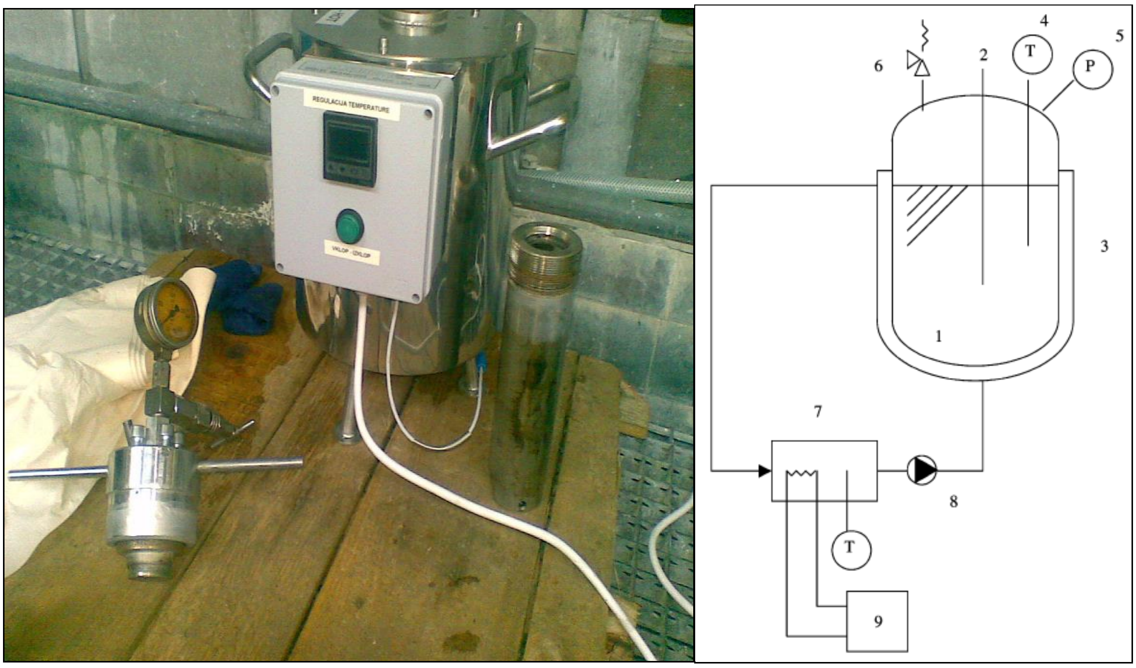


Figure 8. Hydrolysis reactor and experimental set-up: reactor vessel (1) with 200 ml of WAS sample (2); heating shell (3); temperature (4); pressure probe (5); pressure-relief valve (6); thermal block (7); and voltage regulator (9). The applied voltage is controlled by T (4).

- For the concentration optimization, we sampled the WAS from the recycle stream after secondary sedimentation. A daily WAS sample was collected in a 5-L rigid plastic container and carried to the laboratory. The WAS had typically between 15 and 25 g/kg of total dry solids (tDS) and was hydrolysed under predetermined optimal conditions (pH 12, 70 °C) at three concentrations: the original concentration and concentrated to approximately 30.000 mg/L with the help of gravitational sedimentation (24 hours at 4 °C) and thickened to approximately 40.000 mg/L by centrifugation (3500 rpm, 10 minutes). The hydrolysis of the WAS was performed within 24 hours of the sampling.

- The WAS was placed in a 2-L bottle, into which 20% NaOH was added to adjust the pH to 12. It took 11 mL of NaOH for 1 L of original WAS to adjust its pH to 12, 8 mL of NaOH for 1.0 L of sedimented WAS and 7 mL of NaOH for 1 L of centrifuged WAS. The sample bottle was tightly closed to promote the chemical degradation of the organic compounds and to minimize the evaporation of water and volatile compounds. For the hydrolysis temperature of 70 °C, the bottle was placed on a hot stirred plate (Tehtnica Rotomix SHP-10) and heated for the set time of the hydrolysis (1-24 hours) as desired temperature was reached. Longer treatment times were not considered, because of the increase in the energy requirements that these values would imply. During the treatment time the WAS was mechanically agitated with a magnetic stirrer bar to ensure the temperature homogeneity of the WAS sample. The sample without any thermo-alkali hydrolysis treatment was referred to as the blank sample (control).

3.1.3. Analytical methods

- In order to calculate the percentage of solubilisation of organic matter, we measured each time the COD, DS and VS of the total content of the reactor/beaker and of the liquid fraction. The latter was obtained by immediate filtration through a belt-press filter (Figure 9), the size of which is still acceptable for the consequent anaerobic digestion in an UASB reactor. We calculated these parameters for the filter cake as well.

Figure 9. Assembly for press-filtration.

- The COD was measured in a filtrate (the soluble phase) and in a raw WAS sample. The measurements of the DS and VS were determined on the WAS and on the filtrate fraction as well. The solids concentration of a filter cake was calculated from the difference between the DS and VS of the filtrate and raw sample (pDS = tDS – sDS and pVS = tVS – sVS, for dry and volatile solids, respectively). The production rates of the hydrolysis products were defined on a mass-yield basis (COD in mg/kg of sample, DS, MS and VS in g/kg where MS stands for mineral solids and DS = VS + MS). All these concentrations led to the composition in the different parts of the sludge (WAS, LPH-WAS and the filter cake – SPH-WAS). The filter cake was further quantified as the mass % of the total WAS.
- In Section 4.1 we present the results in a comparative manner through trends within the tables and graphs to be able to conclude, by the stationary-phase approximation, which experimental conditions are optimal, i.e., to point out a high enough solubilisation at the shortest possible detention time and the lowest temperature for a favourable pH of the hydrolysis.

3.2. Integration of SPH-WAS into cardboard production

3.2.1. Experimental conditions

To test whether the SPH-WAS is, after the treatment at pH 12, 70 °C for 2 hours, suitable as a raw material for the production of the cardboard, we first tested its hygienisation. Thereafter, we mixed it in different portions (0.5, 1 and 5 mass %) with the common raw materials for the production of the cardboard, i.e., recovered fibres from waste paper and fresh fibres from wood. The cardboard sheets were formed from these mixtures to be able to test the optical and mechanical influence of the SPH-WAS within the raw materials.

3.2.2. Experimental setup

We disintegrated the mixtures of the SPH-WAS with waste paper or fresh fibres into the pulp by mixing them thoroughly. The testing pieces of cardboard were formed from the pulp in a sheet former (Figure 10) according to (ISO5269).

Figure 10. The sheet former.

3.2.3. Analytical methods

To evaluate the hygienisation of the SPH-WAS, indicative pathogens, i.e., total coliforms, Escherichia coli and enterococci, were determined with a presence/absence test (Merck´s Fluorocult® LMX Broth).

The cardboard sheets were analysed with L&W Elrepho SE 070 (brightness), L&W SE 060 (tensile index) and Mullen (burst strength), according to the standard methods (ISO2470) (ISO1924) (ISO2758).

3.3. Pilot plant UASB experiment

3.3.1. Experimental conditions

Based on the results of the basic research on the thermo-chemical hydrolysis of WAS in the first phase, we extended our laboratory experiments with a simulation of the operation on a pilot UASB reactor in the last phase of our research. Before that, we also optimized the hydrolysis of the thickened WAS and thereafter we tested the SPH-WAS for its suitability in cardboard production.

Pilot-scale experiments were performed to confirm the suitability of the laboratory results of the hydrolysis of the WAS at pH 12, 70 °C for 2 hours, and to take into consideration some process characteristics so that the thermo-alkaline hydrolysis can be further technically and economically assessed afterwards.

We tested the anaerobic digestion of the LPH-WAS in a pilot UASB reactor (Figure 11) to find out for which addition of optimally produced LPH-WAS to the pulp-and-paper raw wastewater, organic load, the biodegradability of the mixed substrate and methane production is optimal.

Figure 11. Pilot UASB reactor.

3.3.2. *Experimental setup*

We performed trials with the anaerobic digestion of WAS in a lab-scale pilot plant (Figure 12), which is a simulation of the full-scale Pacques IC reactor that has operated from 2006 in Količevo Karton. Its central part is a cylindrical vessel with a total volume of 12 L, which was filled at the start of the experiment with 6 L of anaerobic biomass from the IC reactor.

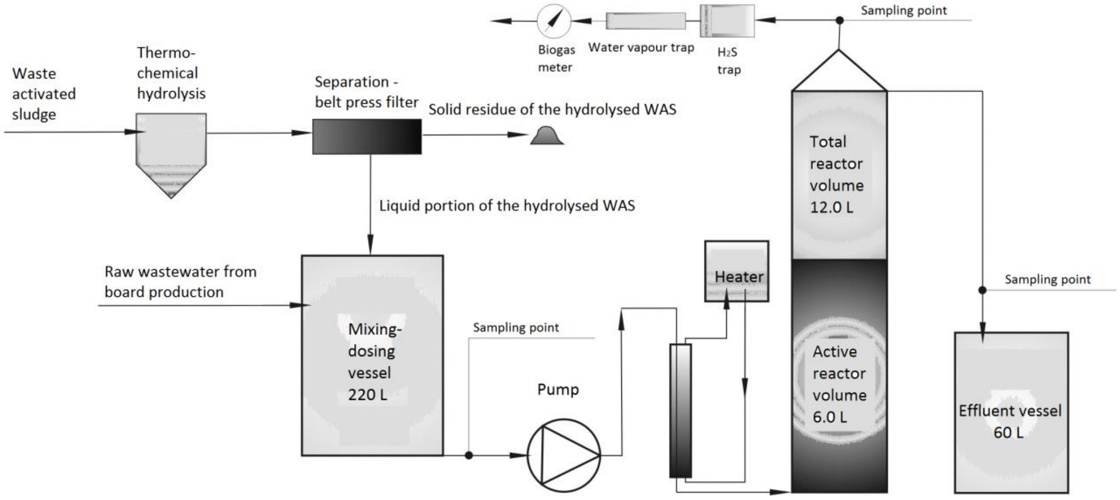


Figure 12. Pilot-plant setup.

For this purpose, the WAS hydrolysis pre-treatment was carried out with simultaneous pasteurization by injecting steam at a temperature of 100°C into a 100-L hydrolysis reactor, mixing it within the WAS, the pH of which was adjusted to 12 (1 L of 20% NaOH for 90 L of WAS), raising the bulk suspension temperature to 70°C and proceeding for 2 hours. The hydrolysis reactor was equipped with valves to control the steam entrance from the boiler and the hydrolysed WAS exit from the reactor to the flash. At the end of the detention time of 2 hours, the exit valve was opened and the hydrolysed WAS was released to the centrifuge. The WAS, which was slightly diluted by the steam condensation, had a pH of 10.0 at the end of the hydrolysis and was as such stored for continuous use in the pilot plant. The LPH-WAS was not neutralized with an acid because it was planned to mix it at a relatively low percentage (3-10 vol. %) with the raw wastewater of a quite low pH of 6.0-6.5. We mixed industrial raw wastewater and the LPH-WAS in a 220-L influent vessel in a ratio based on the available average quantities of the WAS and the raw wastewater of the Karton Količevo (5:100). The raw wastewater addition was screened with a mesh (0.01 mm) to prevent clogging of pilot reactor pipes by the excessive flocculant it contained. As a blank (control) substrate, we fed into the reactor the raw wastewater, which was distributed twice a week from Količevo Karton to the laboratory and stored at 4°C. The pH of raw wastewater was left as is, without any controlled addition of NaOH, and it was increased towards pH 7 only when the LPH-WAS was added. The influent reservoir/feeding tank was mechanically mixed using a stainless-steel paddle on a central shaft operated at a constant speed by an electric motor with a speed controller

(Heldolph mixer system). Based on the reactor's working volume of 12 L, the influent was fed continuously to the reactor at a rate of the set flow (30-200 L/day) using a solenoid-driven, diaphragm-type, metering pump (ProMinent Gamma/4). In this way, the reactor was operated for a hydraulic retention time (HRT) between 1.5 h and 10 h. The temperature of the reactor was kept at 35±3 °C with the help of a heat exchanger preceding the reactor and with a water jacket around the reactor, through which thermostated water circulated (Julabo circulating water bath). The reactor was kept under the same working conditions for a period corresponding to at least three HRT, ensuring steady-state conditions, and maintained for at least ten more HRT for data collection. The produced biogas was led from the top of the reactor into an instrument for the on-line measurement of the volume of the produced gas (flowmeter Agilent ADM 2000), which was continuously recorded using a desktop PC. A gas trap containing a solution of $AgNO_3$ was installed before the instrument to trap the released hydrogen sulphide and a silica gel trap to absorb the water vapour.

3.3.3. Analytical methods

For the evaluation of the anaerobic digestion, the following parameters were monitored in the pilot-plant reactor:

- Influent and effluent: DS, VS and tCOD, pH and temperature;
- Biomass: DS, VS and temperature;
- Biogas: amount of biogas generated, concentration of methane in the biogas.

The DS and VS of the samples were determined according to the standard methods (DIN12879) (DIN12880). The COD was determined by a HACH DR 3900 Colorimeter using a HACH COD HT 200 S reactor.

A WTW Multi 340i pH-meter was used in the pH measurements, while a Meterman TM45 was used for the temperature determination.

4. RESULTS AND DISCUSSION

4.1. Hydrolysis of WAS

To fully determine the most appropriate combination of operating conditions when using thermo-chemical hydrolysis, we combined major governing parameters in the experiments to assess the influence of the time of hydrolysis, its temperature and pH. In order to study the hydrolysis process of the WAS, we performed a series of experiments under various temperatures at two extreme pH values, i.e., 2 and 12. Consecutive experimental sets were carried at 25, 70, 95, 140, 160, 180 and 200 °C. We related all the results to the equivalent property for the 'blank'-untreated WAS sample. The assessment of the overall trends will enable us to come to a conclusion for this first phase of the experimentation. The characteristics of untreated the WAS are shown in Table 1.

Table 1. Characterization of WAS (average +/- SD).

Parameter	Value
pH	7.6 ± 0.2
DS (g/kg)	15.5 ± 1.5
VS (g/kg)	8.5 ± 0.7
MS(g/kg)	7.0 ± 1.1
tCOD (mg/kg)	13150 ± 1790
sCOD (mg/kg)	3612 ± 968

4.1.1. COD solubilisation

We tested the required temperature of the reaction for pH values 2 and 12 in the range from room temperature to 200 °C. During the reaction, we followed the changes of the tCOD and sCOD concentrations to evaluate the WAS hydrolysis. The value of sCOD vs. tCOD, which was corrected for the mass ratio of filtrate vs. total sample and the designated sCOD/tCOD ratio, reflected the effectiveness of the hydrolysis. For alkali and acid hydrolyses, the sCOD/tCOD ratio is illustrated in Table 2 for different times of hydrolysis.

Table 2. sCOD/tCOD ratio for pH 2 and 12 at different temperatures and times of hydrolysis.

pH 2	t(h) of hydrolysis				pH 12	t(h) of hydrolysis			
T (°C)	1	2	3	24	T (°C)	1	2	3	24
25	-	-	-	0.55	25	-	-	-	0.91
70	0.30	0.46	0.53	0.69	70	0.92	0.92	0.93	0.94
95	0.58	0.66	0.65	0.68	95	0.95	0.96	0.96	0.95
140	-	0.64	-	-	140	-	0.89	-	-
160	-	0.66	-	-	160	-	0.85	-	-
180	-	0.69	-	-	180	-	0.86	-	-
200	-	0.76	-	-	200	-	0.78	-	-

Results show that pH 12 is more appropriate for COD dissolution than pH 2. For pH 12, the highest sCOD/tCOD ratio is for hydrolysis at 70 and 95 °C.

For higher temperatures, we stopped the hydrolysis after 2 hours and in Figure 13 the comparison for all the temperatures after two hours of acid- and alkali-hydrolysis is illustrated.

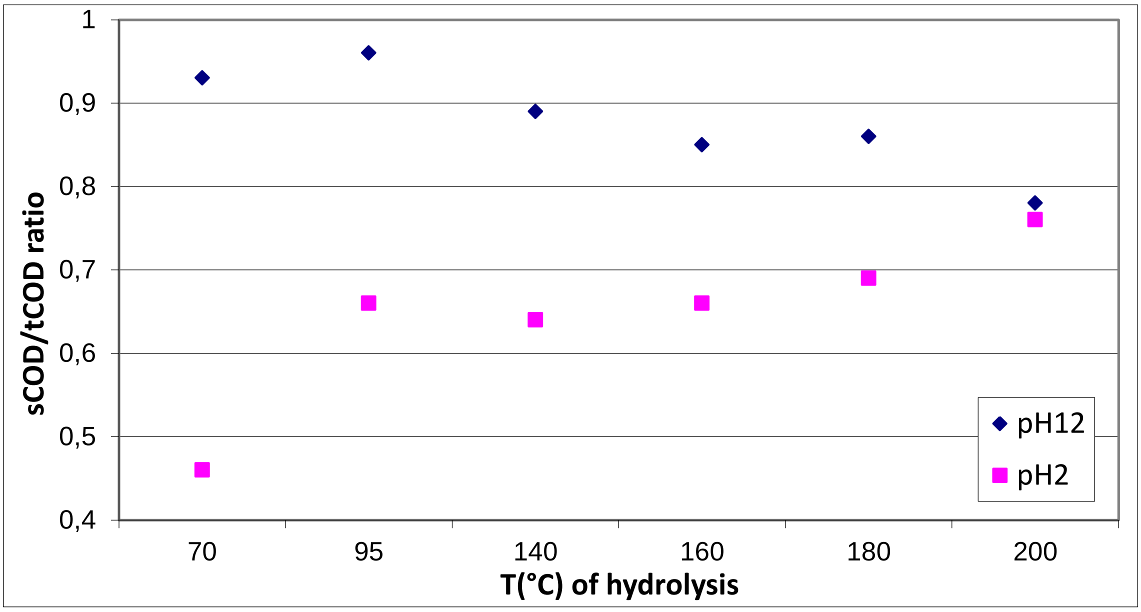


Figure 13. sCOD/tCOD ratio for pH 2 and 12 after 2 hours of hydrolysis for different temperatures.

For the thermal treatment at temperatures ranging from 70 to 200 °C the solubilisation yields decreased with temperature for pH 12 and increased for pH 2. Altogether, they were higher after the thermo-chemical treatments at pH 12 than at pH 2.

The sCOD/tCOD ratio changed only slightly during the first three hours of hydrolysis for two favourable conditions, pH 12 at 70 and 95 °C (Figure 14).

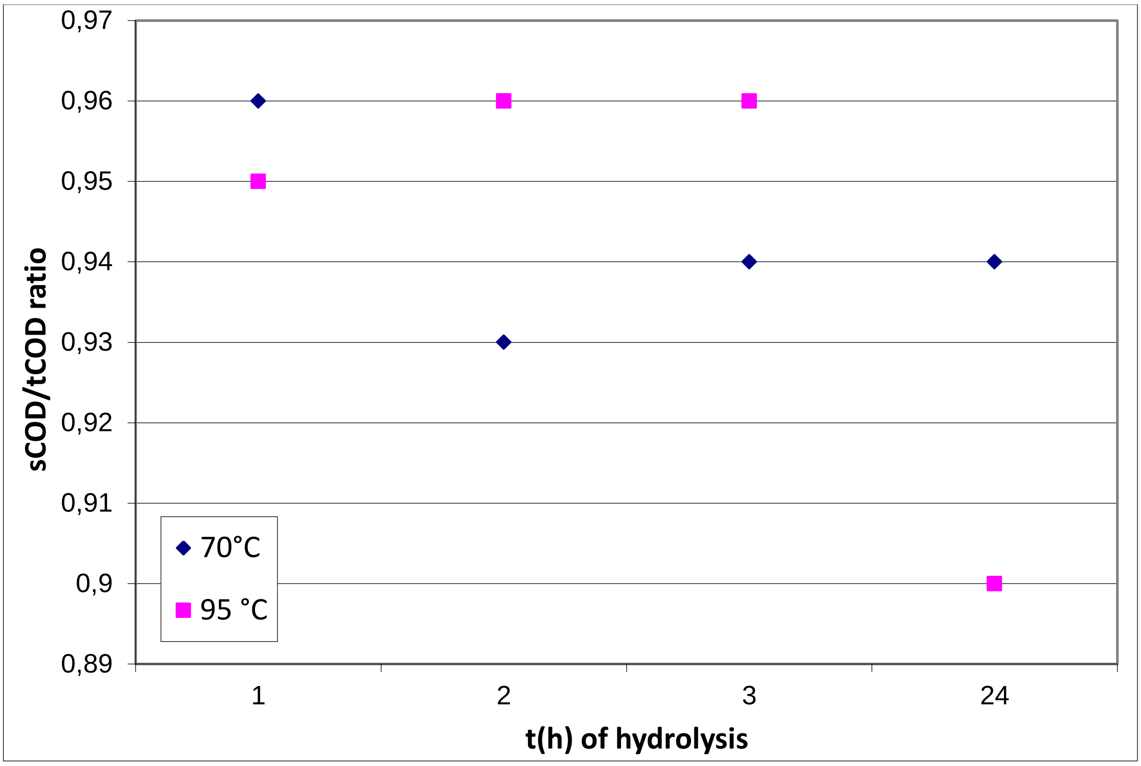


Figure 14. sCOD/tCOD ratio for pH12 at 70 and 95 °C at different times of hydrolysis.

Overall, the WAS hydrolysis rate was more accelerated under alkaline conditions. Except for the highest compared temperature of 200 °C, at all the other temperatures the WAS hydrolysis efficiency was higher in alkaline than in acidic conditions.

Within 24 hours of the hydrolysis, the ratio of absolute sCOD and tCOD remains at a high level for both 70 and 95 °C. As already visible from the comparison of the sCOD/tCOD ratio, the efficiency of COD dissolution under alkaline conditions was higher than that in acidic. The concentrations of sCOD released at pH 2 were appropriately lower.

4.1.2. tDS and tVS

The increase of DS in the filtrate during the hydrolysis was consistent with the increase of sCOD. In Table 3 the effectiveness of their solubilisation is presented as the ratio between sDS/tDS. The same correction with the mass ratio of filtrate and the total sample was applied.

Table 3. Solubilisation of DS for pH 2 and 12 at different temperatures and times of hydrolysis.

pH 2	t(h) of hydrolysis				pH 12	t(h) of hydrolysis			
T(°C)	1	2	3	24	T(°C)	1	2	3	24
25	-	-	-	0.72	25	-	-	-	0.89
70	0.55	0.53	0.61	0.73	70	0.95	0.96	0.95	0.98
95	0.87	0.88	0.86	0.90	95	0.66	0.68	0.68	0.69
140	-	0,81	-	-	140	-	0.77	-	-
160	-	0,78	-	-	160	-	0.70	-	-
180	-	0,77	-	-	180	-	0.68	-	-
200	-	0,85	-	-	200	-	0.57	-	-

The DS solubilisation had its peak values at pH 12 and 70 °C and was decreasing towards higher temperatures at this pH (Figure 15). For pH 2, the lowest values were at 70 °C, while elsewhere the values were higher than at the corresponding temperatures for pH 12, but nowhere reached the maximum of pH 12 and 70 °C.

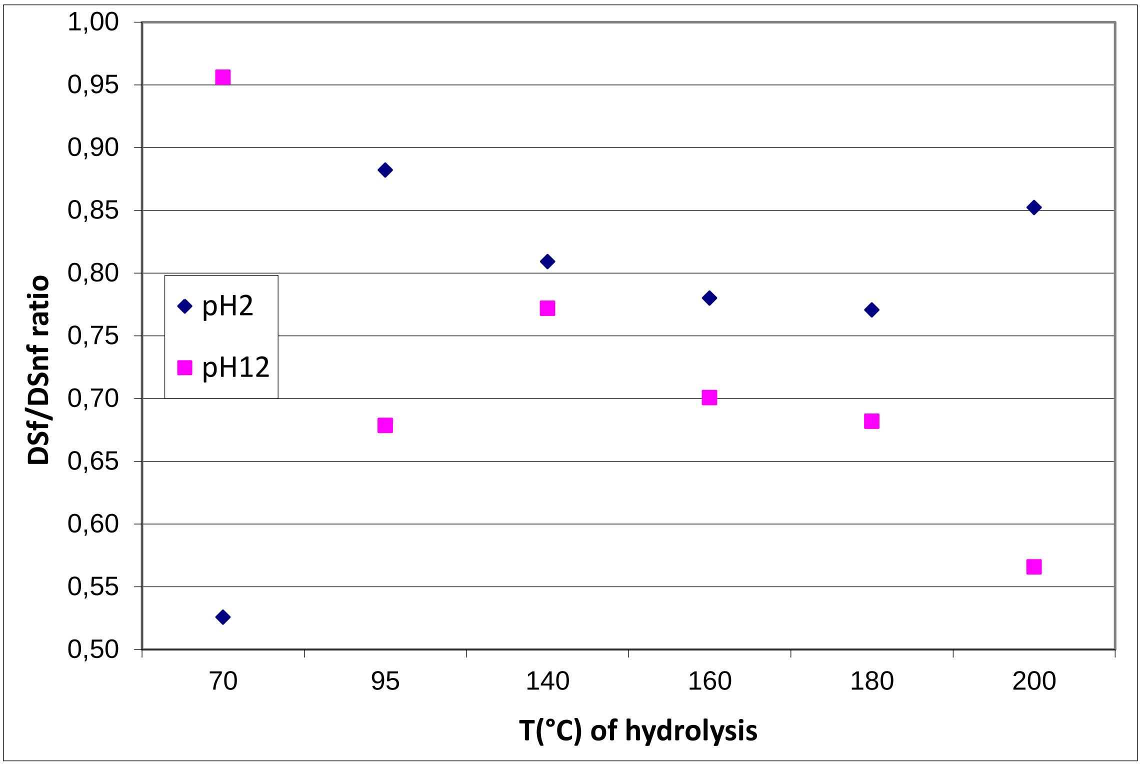


Figure 15. The solubility of DS for pH 2 and 12 after 2 hours of hydrolysis for different temperatures.

Unlike the similarity of the COD solubilisation, the DS solubilisation for pH 12 at 70 and 95 °C was higher at 70 °C (Figure 16).

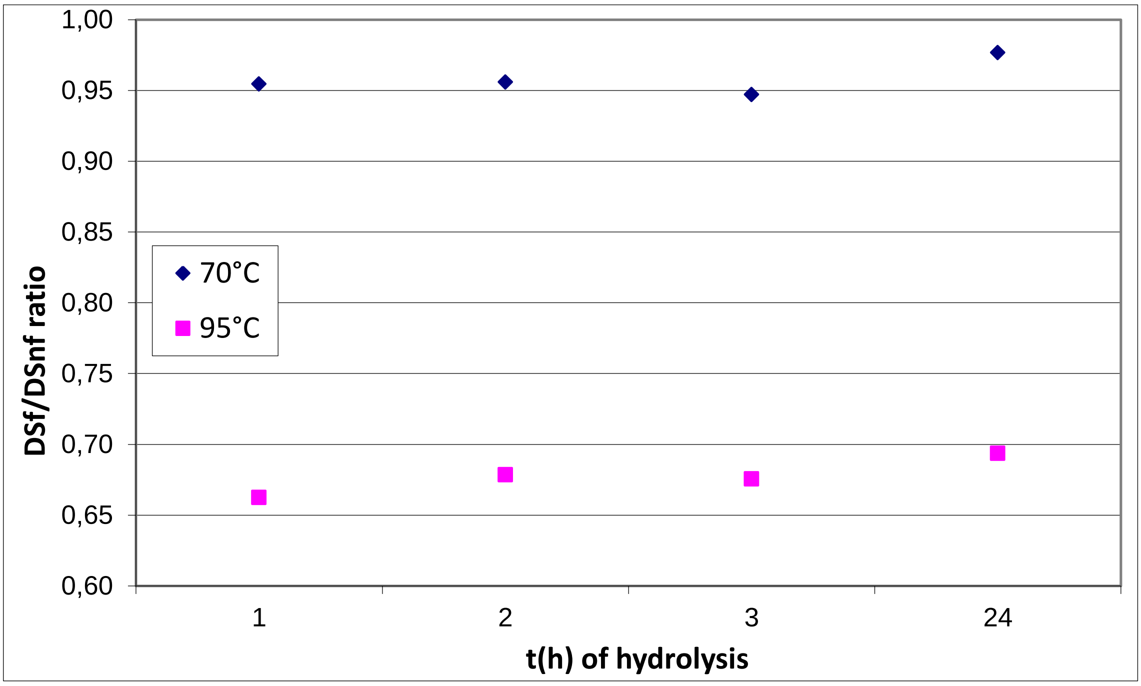


Figure 16. Solubility of DS for pH 12 at 70 and 95 °C with the time of hydrolysis.

The closer resemblance between the solubilisations of MS and COD for pH 12 is illustrated in Table 4.

Table 4. Solubilisation of MS for pH 12 at different temperatures and times of hydrolysis.

pH 12	sMS/tMS			
	t(h) of hydrolysis			
T(°C)	1	2	3	24
25	-	-		0.88
70	0.82	0.84	0.95	0.96
95	0.95	-	-	0.99
140	-	0.81		-
160	-	0.69		-
180	-	0.65		-
200	-	0.57		-

The overall trend showed a lower solubility of the mineral part and a decrease of the solubility towards the highest temperatures.

4.1.3. *Residual solids*

The release of DS in the liquid phase resulted in a reduction of the quantity of filter cake. The ratio of masses of the SPH-WAS and the hydrolysed WAS samples before the press-filtration is shown in Table 5.

In general, a lower mass portion of filter cake was obtained at pH 12, where the residual mass was reduced much more with respect to the one after hydrolysis at pH 2.

To be comparable in this respect with the efficiency of pH 12, the reduction of the SPH-WAS at pH 2 could only be achieved at very high temperature (Figure 17).

Table 5. Mass percentage of residual solids after press-filtration for pH 2 and 12 at different temperatures and times of hydrolysis.

pH 2	t(h) of hydrolysis				pH 12	t(h) of hydrolysis			
T(°C)	1	2	3	24	T(°C)	1	2	3	24
25	-	-	-	5.8	25	-	-	-	6.6
70	8.3	10.8	7.4	8.4	70	2.4	4.8	4.4	4.6
95	8.1	8.3	10.6	10.1	95	4.0	4.2	3.9	n.a.
140	-	5.7	-	-	140	-	1.5	-	-
160	-	5.3	-	-	160	-	3.3	-	-
180	-	3.5	-	-	180	-	4.2	-	-
200	-	6.2	-	-	200	-	2.3	-	-

n.a. indicates where a non-plausible result was rejected

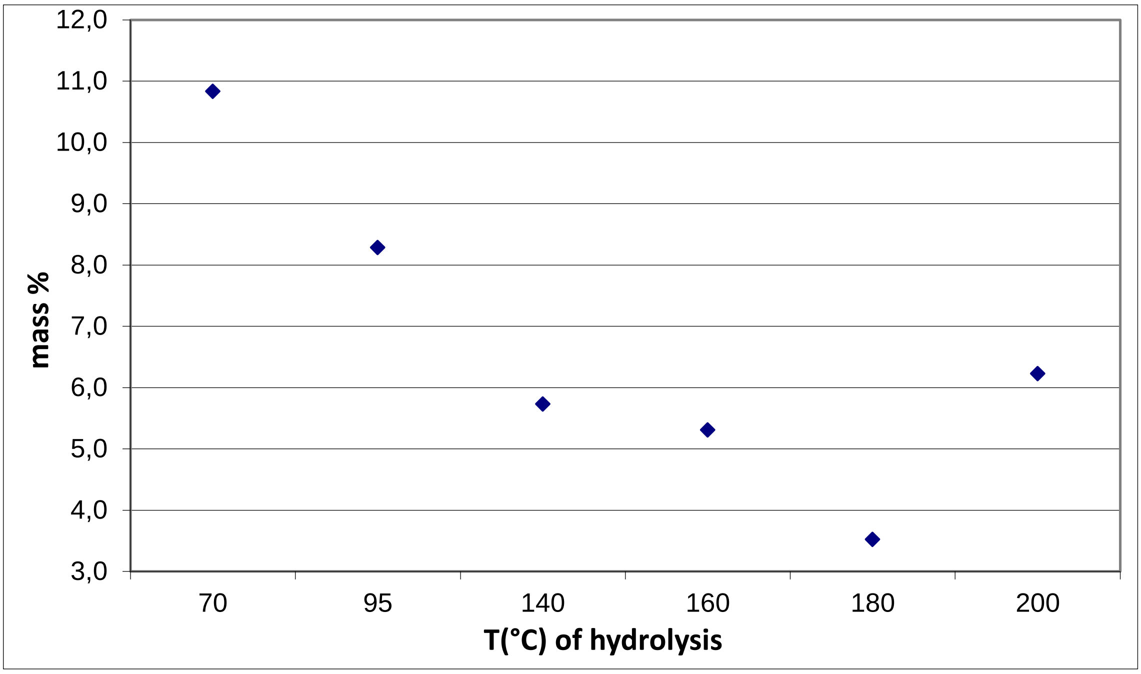


Figure 17. Filter-cake mass % for different temperatures after 2 hours of hydrolysis at pH 2.

Press-filtration proceeds to the lowest SPH-WAS amount for pH 12 at temperatures of hydrolysis that are also higher than 95 °C (Figure 18). At 140 °C, the filter-cake amount was with 1.5 mass % more than halved with respect to 4.2 mass % at 95 °C. Nevertheless, already 4.2 mass % at 95 °C represents a significant reduction (58 %) from approximately 9.9 ± 0.4 mass %, which is characteristic for untreated WAS.

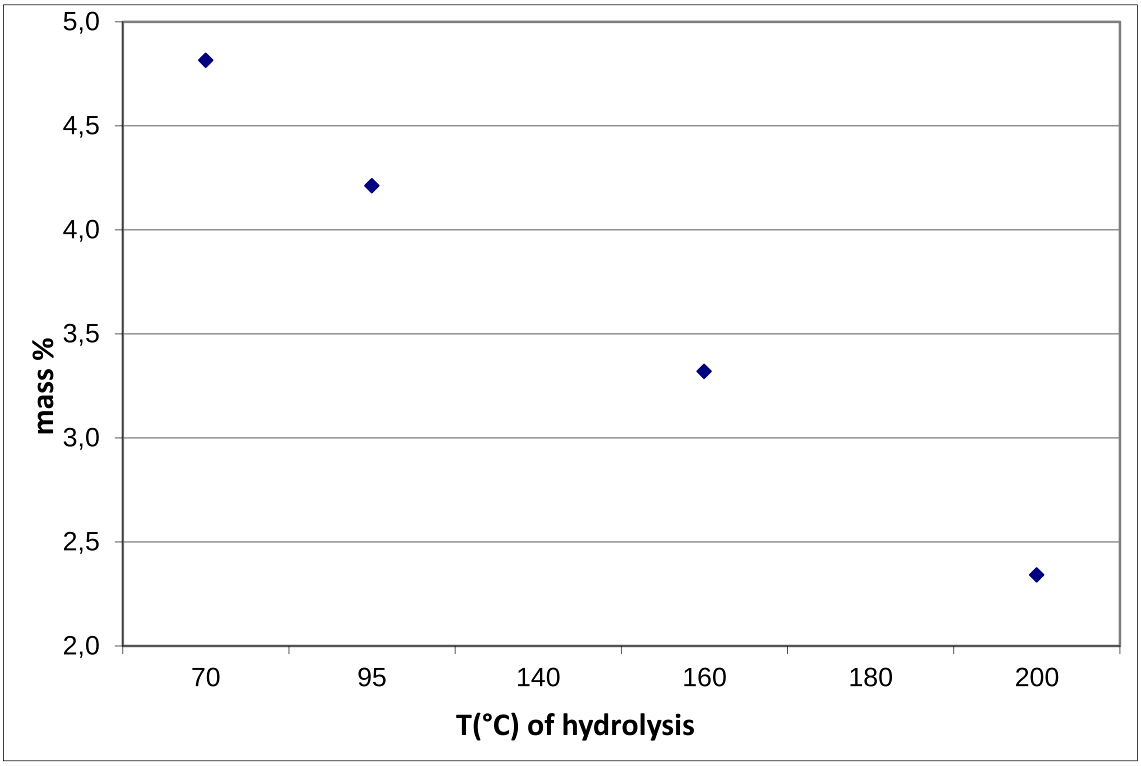


Figure 18. The trend of filter-cake mass % for hydrolysis at pH 12 after 2 hours at different temperatures.

The percentage of DS in the filter cake is also higher at pH 12 than at pH 2.

The supernatant after hydrolysis with pH 12 was more turbid than before it (Figure 19), which indicated that more small molecular compounds were produced after the pretreatment, resulting in the colloids and dissolved solids. These remained in the supernatant and were not removed by press-filtration and settling.

Figure 19. Settling (1 hour at 4 °C) of particles in a series of hydrolysed samples at pH 12 and 95 °C. The first (1) is the original WAS, followed by samples hydrolysed for different times up to 24 hours (2-8): 0, 1, 2, 3, 4, 18 and 24 hours.

4.1.4. *Stability of pH during hydrolysis*

Considering the effect of the pH of the medium, we measured the pH during the hydrolysis when the sampling was done. During the acidic hydrolysis, the pH remained constant, while it dropped in the alkali case (Figure 20).

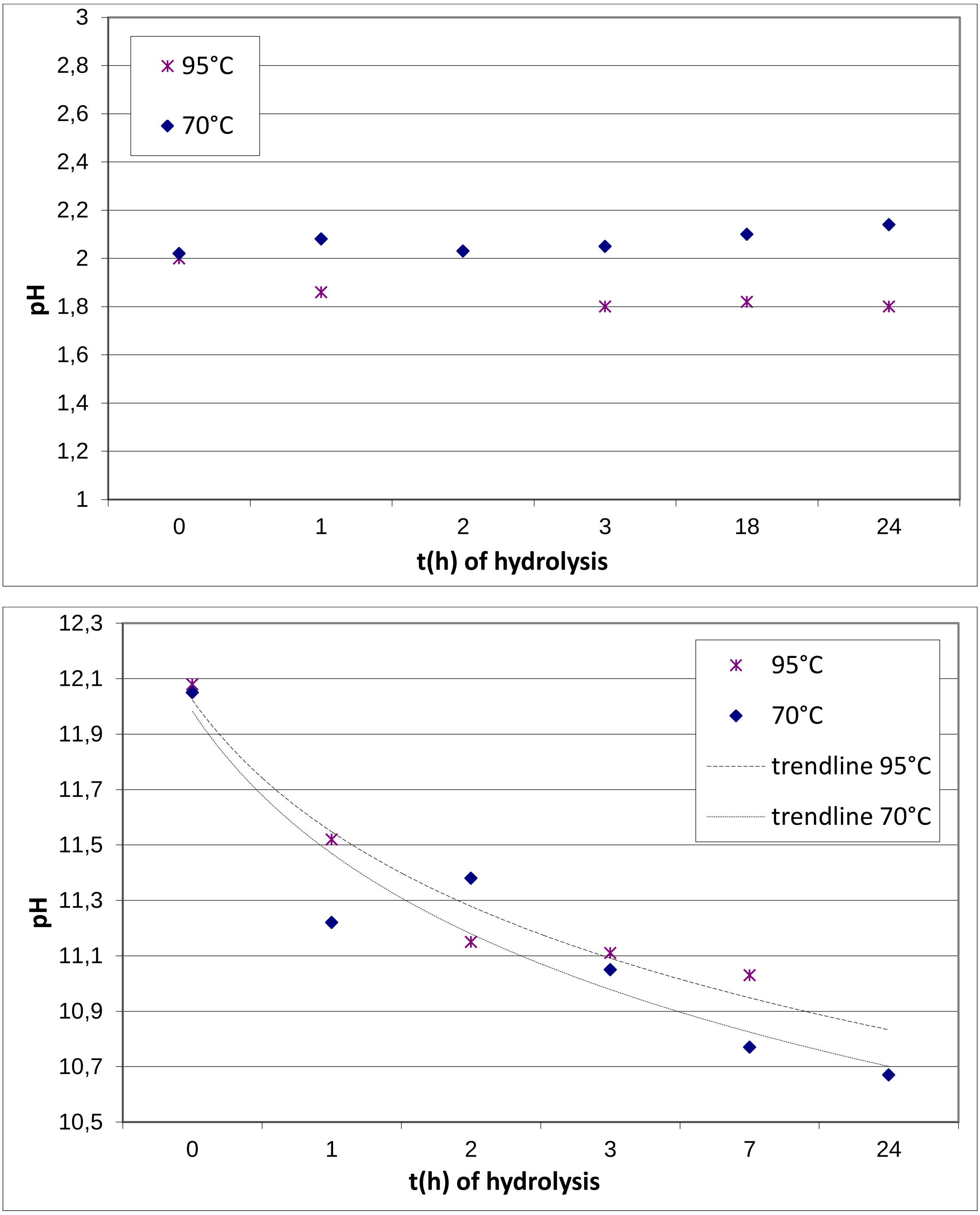


Figure 20. pH of unfiltered samples for starting pH 2 (above) and 12 (below) at 70 and 95 °C. Precision of pH-meter is ±0.03 units.

In the case of alkali hydrolysis, the pH decreased due to the dissolution of organic acids and the consequent neutralization.

4.1.5. Discussion and further work

From the perspective of the scientific problem, our research comes down to the following points of interest. How to overcome the limited anaerobic digestion of the WAS as a solid substrate, which itself is not easily biodegradable? How to realize within an acceptable time and economic frame an effective hydrolysis as the limiting step of the anaerobic digestion of WAS? What are the appropriate hydrolysis conditions to achieve the above goal?

Firstly, we have chosen the thermo-chemical approach. To study the efficiency of the thermo-chemical pre-treatment of the WAS from the pulp-and-paper mill, we analysed the following parameters: sCOD/tCOD, DS/MS/VS of WAS, filtrate and filter cake, together with its mass balance. Whether these parameters can ever fulfil the criteria of time and economics, is determined by the nature of the WAS. The first phase of our research revealed that a successful combination of pH, temperature and duration of hydrolysis can yield successful resuts.

pH

From the two chosen pH extremes for the hydrolysis, i.e., pH 2 and 12, the latter enabled better solubilisation of the WAS. The ratio sCOD/tCOD, as a primary indicator of hydrolytic efficiency, showed that at temperatures from room to 140 °C, pH 12 is more effective than pH 2. After 2 hours at pH 12, the sCOD/tCOD reached 0.89 at 140 °C, while at pH 2 it was only 0.64. The acid addition showed better sCOD/tCOD ratios at higher temperatures, from 160 to 200 °C, where it reached a maximum of 0.76, while sCOD/tCOD at pH 12 and temperatures above 140 °C decreased to a minimum of 0.78 at 200 °C. With respect to the energy and financial criteria, a lower temperature is preferred. Also in this respect, pH 12 is our choice. Furthermore, the costs for sodium hydroxide and hydrochloric acid for such extreme pH value of hydrolysis and re-neutralization could be reduced with the use of acidic wastewater, which is a by-product in thermal-power plant cleaning at Količevo Karton.

Temperature

At the favoured pH 12, the temperature for hydrolysis was more important than the contact time, and it seemed to govern the extent to which the WAS solubilisation occurred. For 70 and 95 °C, the sCOD/tCOD ratio had approximately 95% and remained within a few percent after 1, 2 and 3 hours of hydrolysis. The variation of the sCOD/tCOD ratio was then larger between different higher temperatures. It varied gradually from a maximum of 96 % at 95 °C to a minimum of 78 % at 200 °C after 2 hours of hydrolysis. We decided to continue with pH 12 and 70 °C.

Besides the economic motivation for the lower temperature, at higher temperatures as well a reduction in the biodegradability of the solubilized WAS could occur due to refractory compounds which are known to be formed above 170 °C and do not easily degrade (Bougrier, et al., 2007). A higher sCOD in this respect would not mean automatically higher anaerobic degradation and the well-known linear relationship between the solubilisation and the biodegradation. Otherwise, all the organic material from pulp-and-paper production can be anaerobically digested, except for stable woody materials since anaerobic micro-organisms have difficulty in degrading lignin.

Detention Time

A short enough time of hydrolysis and subsequent anaerobic digestion present a major challenge for any system where care has to be taken for a significant amount of WAS. A fast and effective hydrolysis of WAS as a limiting process means at the same time faster anaerobic digestion. In low enough temperature range, sodium hydroxide addition leads to effective organics solubilisation through the destruction and dissolution of the cell mass, which would otherwise be protected by the cell membrane, slowly degradable in anaerobic digestion. In our case, 1 hour of hydrolysis was enough for the combination of pH 12 and 70 °C to ensure the sCOD/tCOD ratio of 96 %.

WAS reduction

The supernatant of the WAS hydrolysed at pH 12 appeared more turbid that the one under acidic conditions or the one of untreated sample. The settled WAS flocks were of reduced quantity. The filter cake remained below 4.6±0.2 mass % of the WAS quantity after the hydrolysis at pH 12 and 70 °C. Compared to 9.9±0.4 mass % in the case of raw

WAS, this represents a 55% reduction. Although at higher temperatures the filter-cake portion was even lower, down to 1.5 mass % of WAS, the present problem of remaining solids can be substantially reduced at pH 12 and 70 °C after a few hours of hydrolysis. Besides improving the digestibility potential and reducing the quantity of residual solids, the benefit of the destruction of pathogenic organisms in the residual solid waste at pH 12 and 70 °C also has to be considered. This would make SPH-WAS usable as a secondary raw material in cardboard production at Količevo Karton.

Further work

The combination of pH 12, a temperature of 70 °C and the time of hydrolysis from 1 to 24 hours proved that we can overcome the limitations of WAS: low overall degradation efficiency of its organic dry solids (30–50 %) and long detention times for anaerobic digestion (20–30 days) (Chen, et al., 2007). A longer detention time and/or higher temperature would increase the installation costs, because of the extra energy demand and the larger volume of the hydrolysis tank. Considering the latter, we have within the second phase of our research searched for the optimal concentration of WAS influent for the hydrolysis reactor and for the optimal time connected to it. For this purpose, the WAS was concentrated to approximately 30 and 40 mg/l by sedimentation overnight at 4 °C and by centrifugation, respectively, and hydrolysed at pH 12 and 70 °C for two consecutive hours. On a large scale, this would mean a gravitational pre-sedimentation, which can be considered as an inexpensive upgrade.

4.1.6. Concentrating the WAS - Starting values of tDS, tVS and tCOD

In the second phase we proceeded with testing the hydrolysis further at three different concentrations of WAS, the characteristics of which are shown in Table 6. Namely, a higher WAS concentration would in practice decrease the volume to be treated and thus the chemicals as well as the energy required for heating, mixing and pumping.

Table 6. tDS, tVS and tCOD of samples of the WAS (control).

Sample	Original	Sedimented	Centrifuged
pH	7.45 ± 0.14	7.46 ± 0.14	7.60 ± 0.04
tDS (g/kg)	25.1 ± 0.5	28.6 ± 0.6	41.8 ± 0.6
tVS (g/kg)	11.5 ± 0.6	13.7 ± 0.7	22.3 ± 0.9
tCOD (mg/kg)	17381 ± 501	23927 ± 2670	29491 ± 2057

The WAS production in the wastewater-treatment plant of Količevo Karton is not constant, neither are its characteristics, since cardboard production is varying as well as the amount of the raw wastewater treated. WAS makes up a major part of the wastewater sludge, besides the primary sludge, which is recycled back to the cardboard production as the filler for the middle layer. For similar use, WAS would have to be hygienised, which could also be accomplished by hydrolysis if the conditions are appropriate. Simultaneous solubilisation of its organics could be used as the feed for existing anaerobic digestion reactor for boosting the biogas production.

For this purpose, we will next test how much of SPH-WAS will be available and whether it could be used as a raw material for the production of the cardboard.

4.1.7. Concentrating the WAS - Difference in sCOD, sDS and sVS before and after hydrolysis

For our original, non-concentrated, WAS, the sCOD/tCOD ratio as the indicator of the solubilisation of the WAS increased from 0.36 to 0.90 after 1 hour of hydrolysis at pH 12 and 70 °C and to 0.94 after 24 hours, which was an increase of 150% and 161%, respectively. The effectiveness reached the top for the intermediate concentration, while for the highest concentration the effectiveness was the lowest (Table 7).

Table 7. sCOD/tCOD ratio of the WAS hydrolysed at pH 12 and 70 °C.

sCOD/tCOD	Sample		
Hydrolysis time (h)	Original	Sedimented	Centrifuged
0	0.36	0.35	0.42
1	0.90	0.94	0.81
24	0.94	0.97	0.84

Similar trend as for the COD was also confirmed by the changes of the soluble dry solids (sDS) and the soluble volatile solids (sVS), which happened in a similar way (Table 8 and Table 9).

Table 8. sDS/tDS of the WAS hydrolysed at pH 12 and 70 °C.

sDS/tDS	Sample		
Hydrolysis time (h)	Original	Sedimented	Centrifuged
0	0.32	0.37	0.35
1	0.92	0.91	0.81
24	0.95	0.99	0.87

Table 9. sVS/tVS of the WAS hydrolysed at pH 12 and 70 °C.

sVS/tVS	Sample		
Hydrolysis time (h)	Original	Sedimented	Centrifuged
0	87.6	83.4	73.6
1	91.6	93.0	79.1
24	93.5	96.5	84.1

Concentrating the WAS by gravitational sedimentation and the following hydrolysis at pH 12 and 70 °C can be considered as an efficient solubilisation pre-treatment of the WAS to reduce its quantity and to solubilize it for the following anaerobic digestion. It is even not necessarily longer than 1 hour. The literature distinguishes (Vlyssides, et al., 2004) in hydrolysis under medium temperature and alkaline conditions between two characteristic phases: a rapid initial phase of one hour duration and a subsequent slower phase that follows a first-order kinetic model. The interest for further hydrolysis is thus limited by the first phase because the sCOD reaches the concentration that is very close to the tCOD of the initial WAS. Also, a longer detention hydrolysis time would lead to higher installation and operation costs, because of the larger volume of the hydrolysis tank

Considering the effect of the pH of the medium, we measured the pH at some points during the hydrolysis when the sampling was done. The expected decrease of the pH is shown in Figure 21.

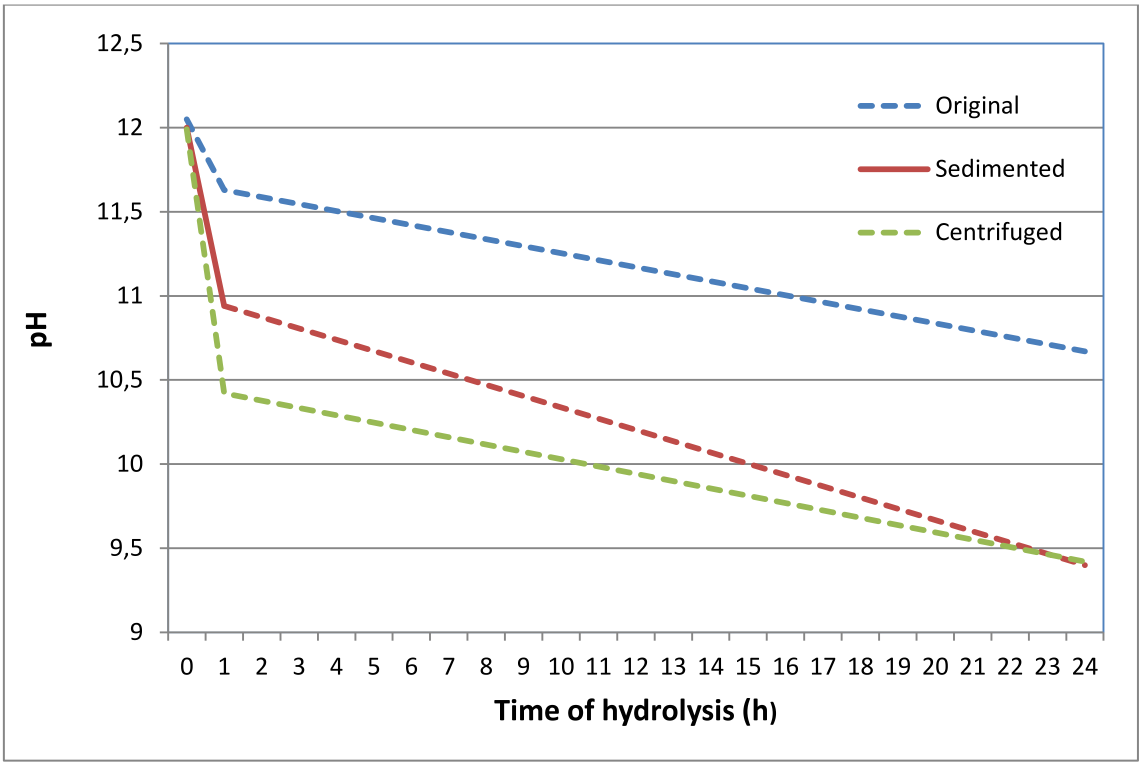


Figure 21. pH drop during hydrolysis at 70 °C.

From a practical point of view, this means that neutralisation is needed before the LPH-WAS enters the anaerobic digestion. It can be achieved partially by mixing the LPH-WAS with the raw wastewater from the cardboard production, which has a typical pH of 6.0-6.5. For the final correction, hydrochloric acid can be applied.

4.1.8. Concentrating the WAS - Reduction of SPH-WAS

Table 10 shows the properties of the filter cake, dewatered by the press-filtration.
The original raw WAS has the lowest mass percentage of filter cake, while the increase visible for sedimented and centrifuged WAS is in the line with their thickening pre-treatment. After the hydrolysis of all three WAS samples, the increase of the soluble chemical oxygen demand (sCOD) caused the amount of filter cake to be decreased as a

result of the progressive solubilisation of organic materials present in the flocks (Figure 22).

Table 10. Characteristics of unhydrolysed WAS.

	WAS Sample		
Property	Original	Sedimented	Centrifuged
%m/m WAS	14.0	18.0	19.5
DS(g/kg Filter Cake)	107	107	129
VS(g/kg Filter Cake)	61.7	61.0	77.2
DS(g/kg WAS)	15.0	19.3	25.1
VS(g/kg WAS)	8.6	11.0	15.0

The largest reduction of filter cake with respect to raw WAS (control) happened within the least concentrated original WAS - 76% and 86% reduction after 1 and 24 hours of hydrolysis detention time, respectively. In addition, already by adjusting its pH to 12 and before reaching 70 °C, the reduction of the filter cake is notable, i.e., 73%. Recalculated to 100 g of original WAS before thickening, the reduction of the filter cake in the sedimented and centrifuged samples is higher by factors of 1.3 and 1.9, respectively, but the remaining amounts of filter cakes after 1 hour of hydrolysis are with 4.8 and 6.4 g per 100 g of original WAS still higher than 3.3 g of the original WAS.

Correspondingly, also the dry and volatile suspended solids (pDS = tDS – sDS, pVS = tVS – sVS; particulate = total - soluble) concentrations have decreased (Figure 23 and Figure 24).

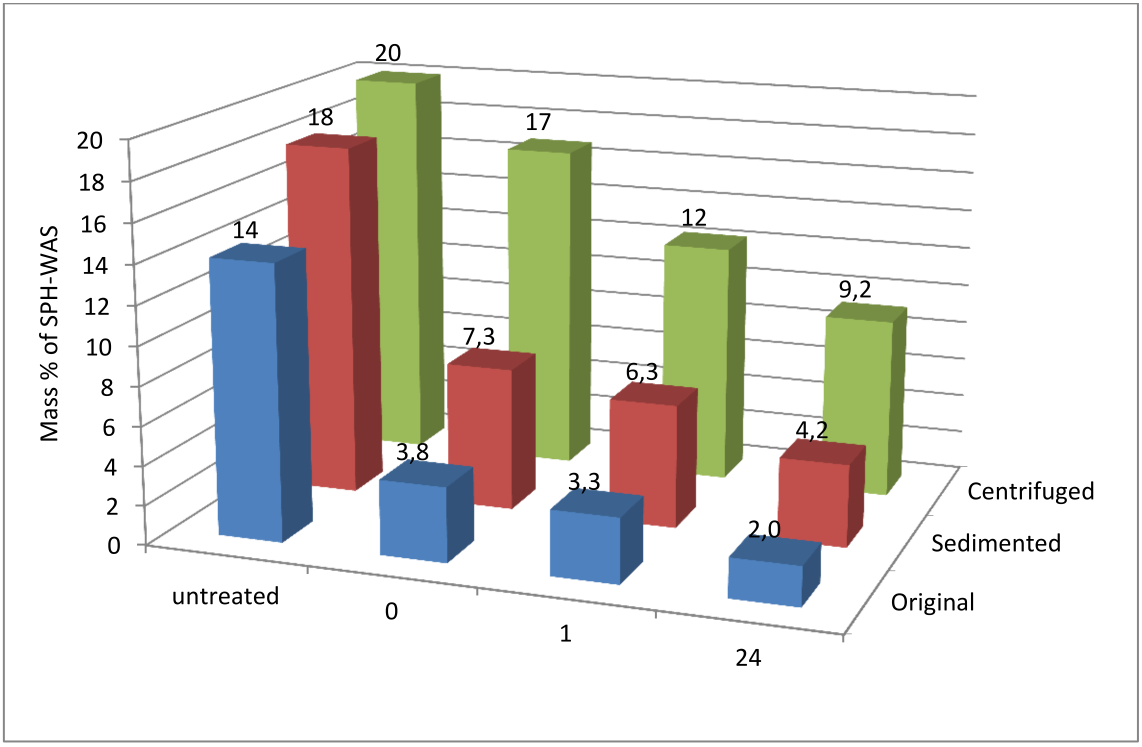


Figure 22. Mass percentage of filter-cake residue from the sludge, SPH-WAS. The horizontal labels mark the untreated sample at the starting neutral pH and the treated samples at pH 12 before hydrolysis and after 1 and 24 hours of hydrolysis.

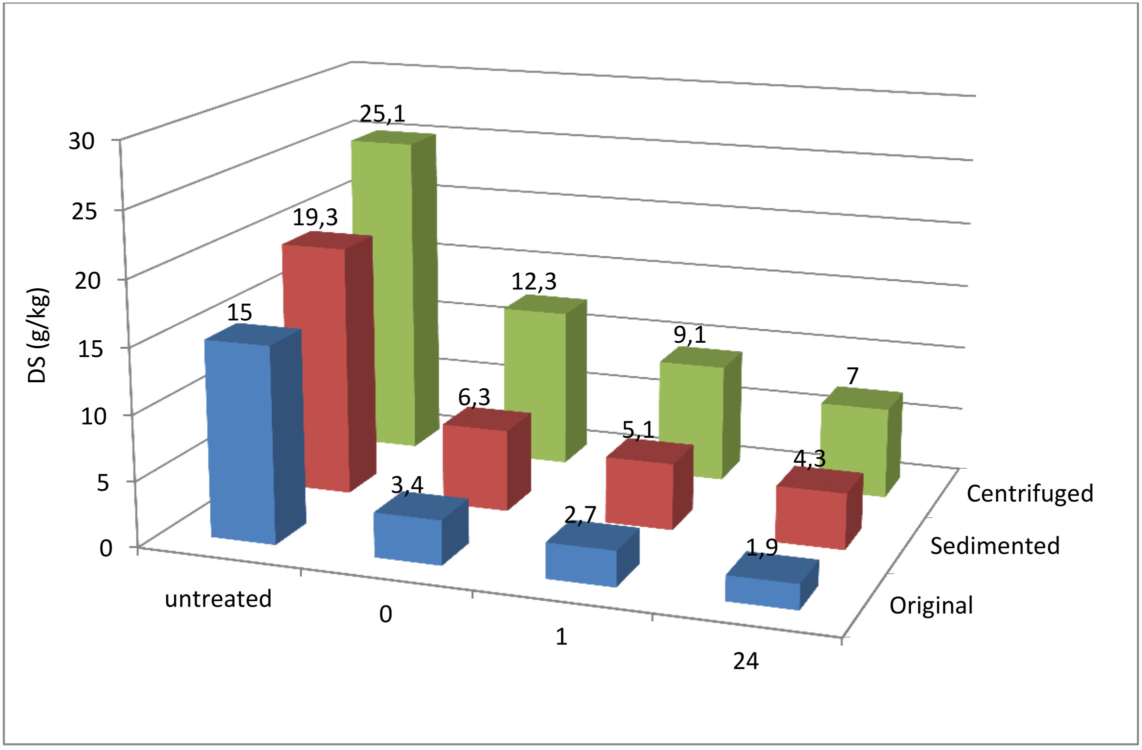


Figure 23. pDS in g per 1000 g of unthickened and the two thickened WAS samples.

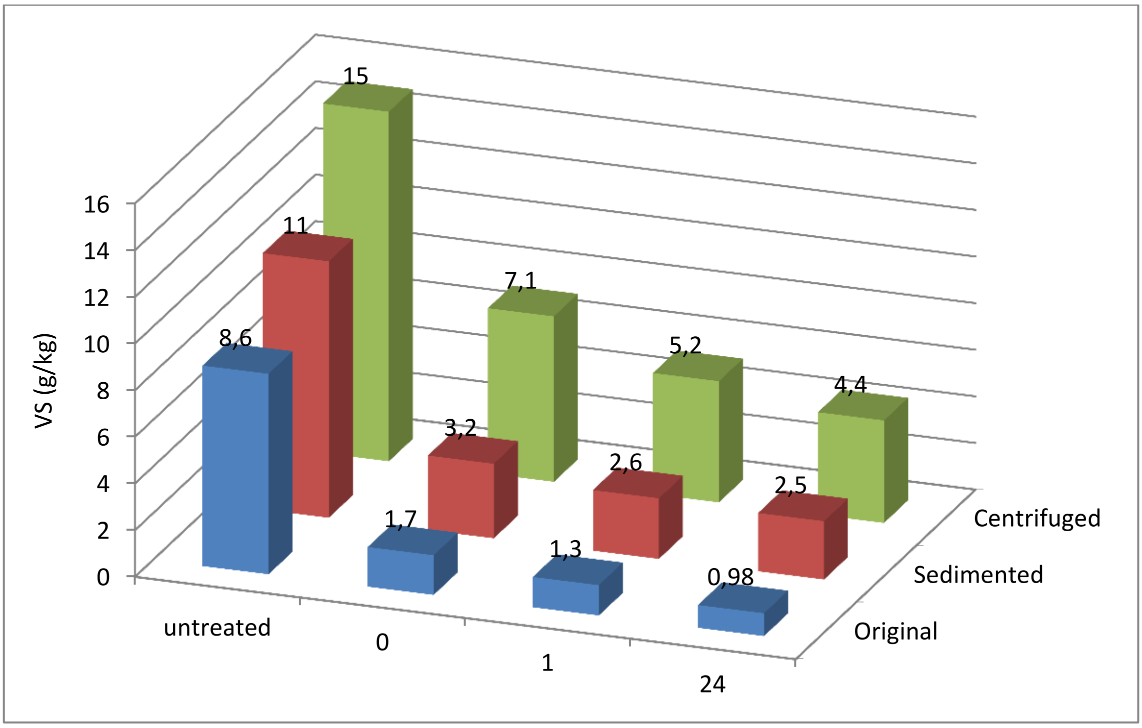


Figure 24. pVS in g per 1000 g of unthickened and the two thickened WAS samples.

Figure 25 and Figure 26 show recalculated to 1000 g of original WAS before thickening.

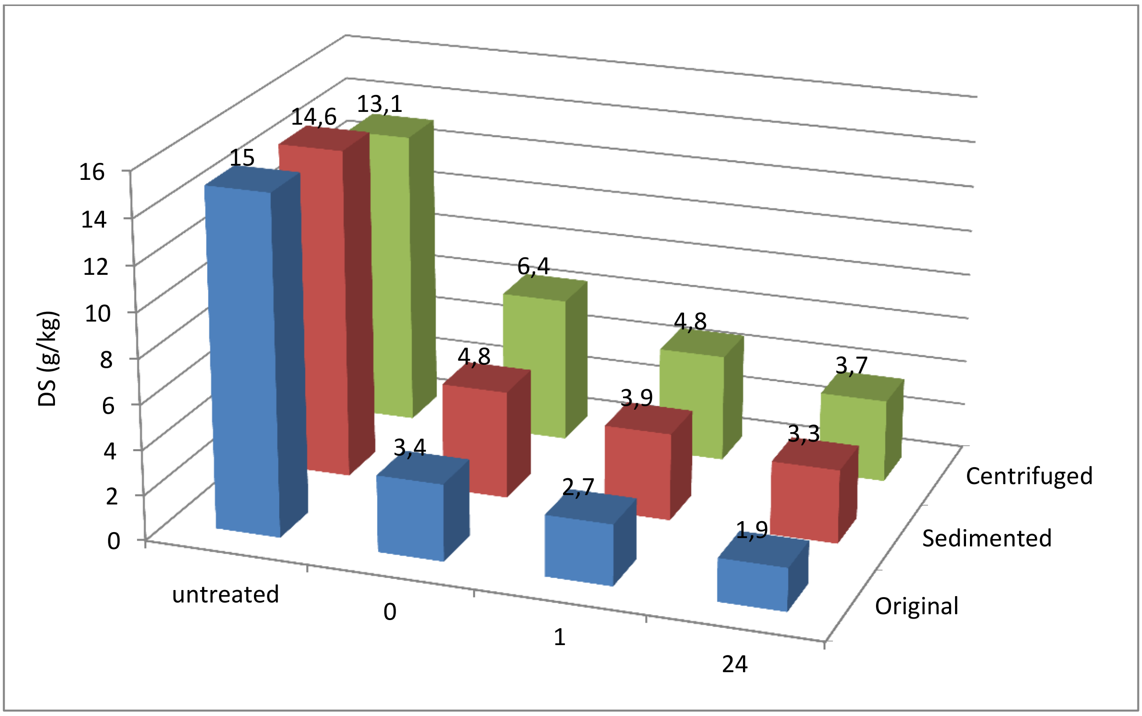


Figure 25. pDS in g per 1000 g of initial WAS suspension before thickening with sedimentation or centrifugation.

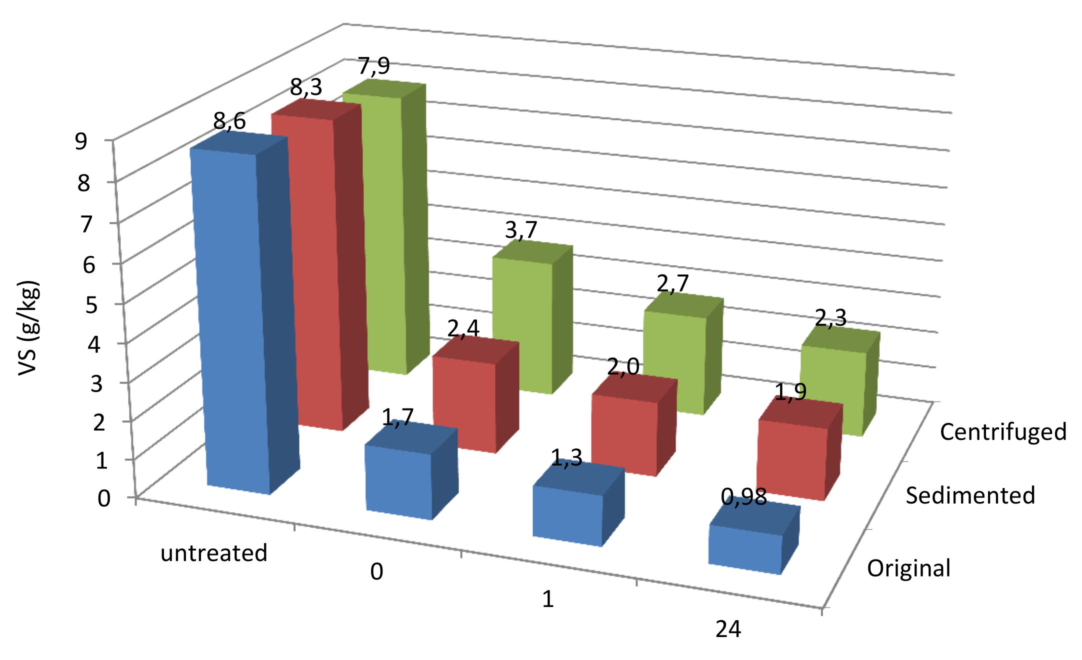


Figure 26. pVS recalculated in g per 1000 g of initial WAS suspension before thickening with sedimentation or centrifugation.

On the other hand, the DS and VS concentration within the filter cake is lower in all cases, the humidity is higher (Figure 27 and Figure 28).

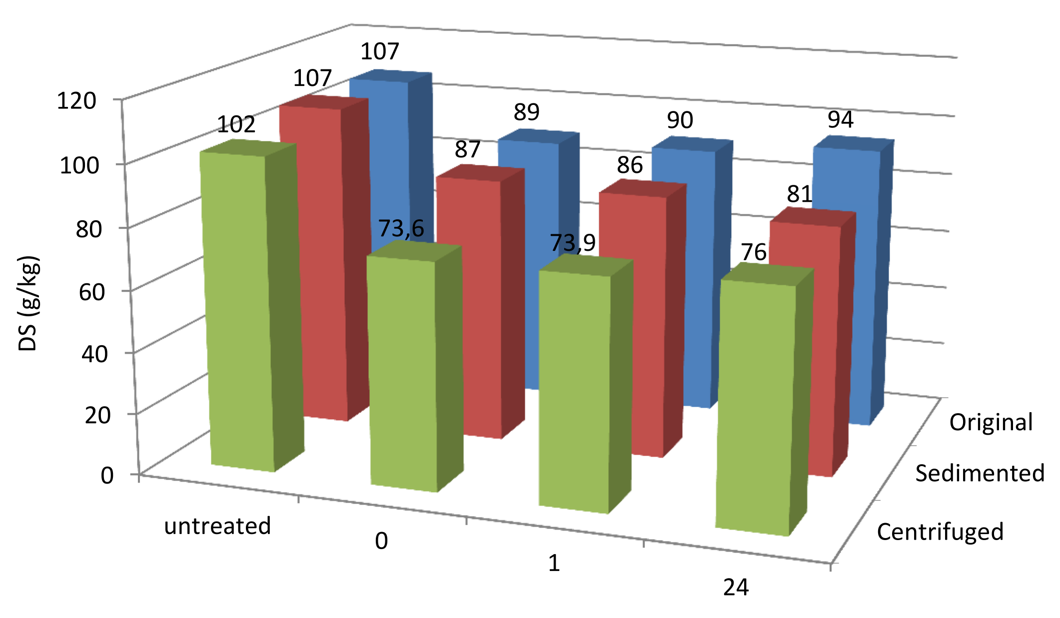


Figure 27. DS in g per 1000 g of filter cake residue.

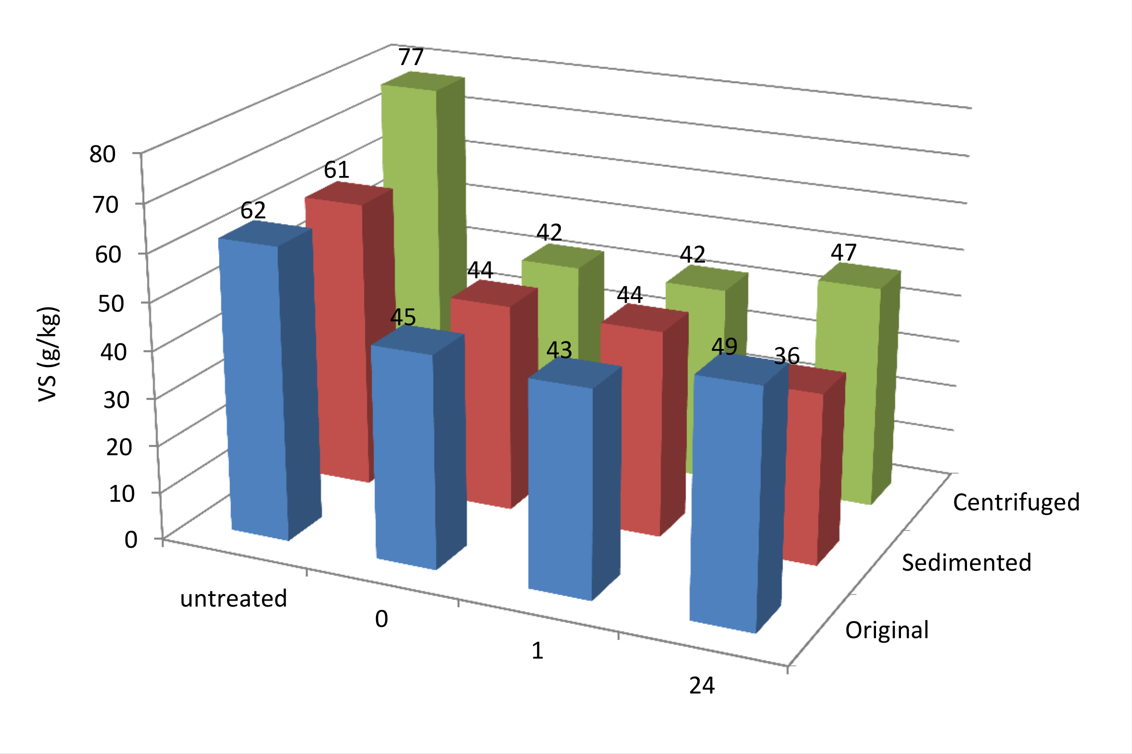


Figure 28. VS in g per 1000 g of filter cake residue.

This is in accordance with the literature (Neyens, et al., 2003), which revealed that excess sodium in activated-sludge systems caused deterioration in dewatering and settling (Figure 29). It was thought that the poor dewatering and settling that occurred with high sodium concentrations was a result of ion-exchange processes in which divalent cations of calcium were displaced from within the flock by the sodium. The monovalent cations reduce the strength of the bonds, and this leads to a loose structure, often decreasing the flock density and the flock resistance to shear. Reduced dewaterability could then be caused by the clogging of the filter by finer material. We have investigated how this affects the incorporation of SPH-WAS into the formation of a cardboard sheet, but first we have to prove that the prerequisite, the raw material hygienisation, was accomplished through the hydrolysis.

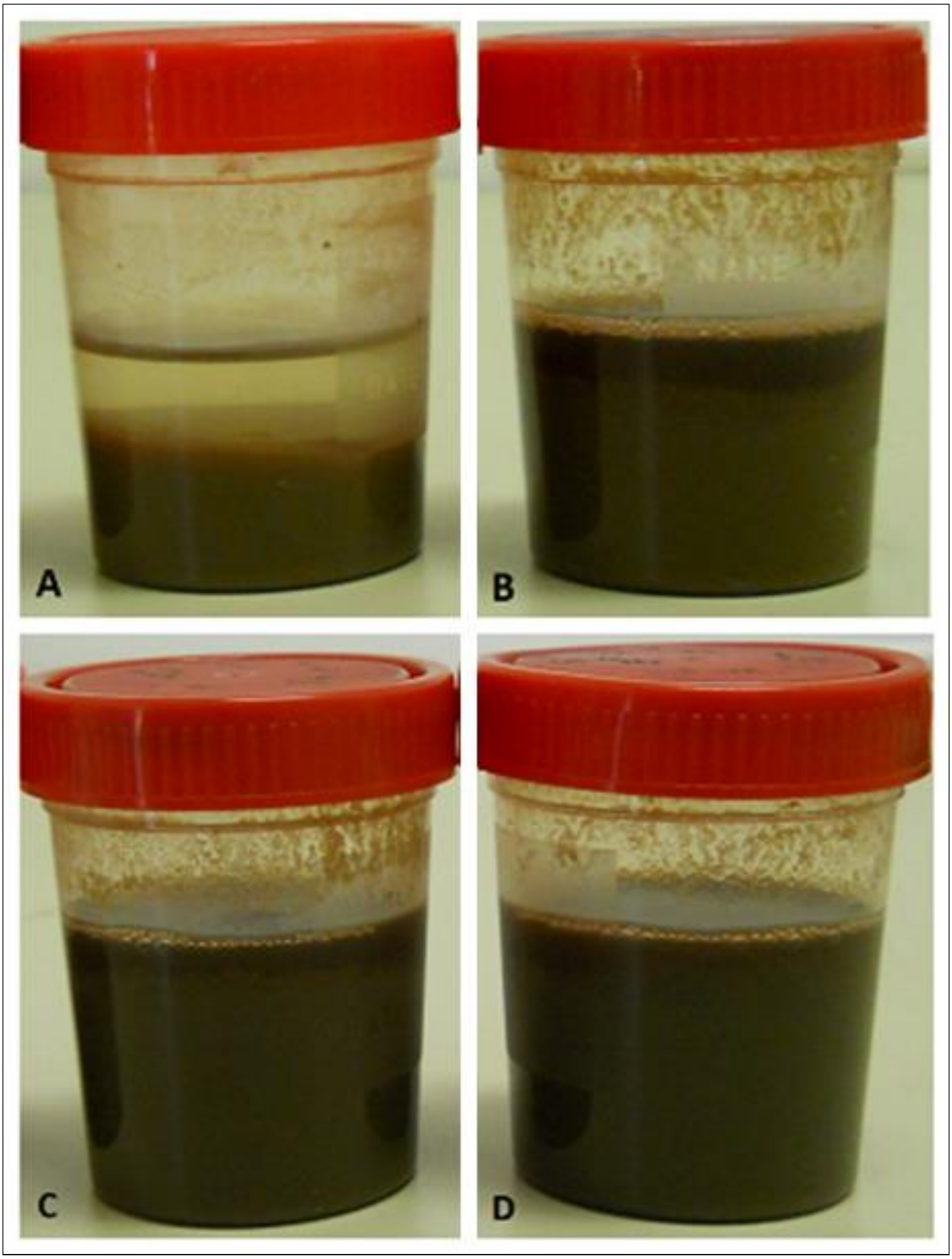


Figure 29. Overnight settling of WAS: untreated sample at starting neutral pH (A) and treated samples at pH 12 before hydrolysis (B) and after 1 (C) and 24 hours (D) of hydrolysis.

4.1.9. Discussion

To test various combinations of pH, temperature and time, as the main factors of the hydrolysis, we hydrolysed the WAS from the biological wastewater-treatment plant of the cardboard producer Količevo Karton at two extreme pH values, pH 2 and 12, in the temperature range from room temperature to 200 °C for an hour up to several days. pH 12 was more efficient than pH 2, according to the level of dissolved organic material expressed as the ratio sCOD/tCOD. It reached over 0.9 after just 1 hour of hydrolysis at 70 °C, which proved to be the most suitable temperature.

NaOH was already proven as suitable dissolving reagent for the hydrolysis of the WAS in many studies. Mahmood and Elliot (2006) stated that a pulp-mill WAS for disposal can be reduced by 70–80 % by alkali digestion and returning the solubilised fraction back to the aeration basin. The investigation on the effect of temperature, alkali concentration and contact period showed that even under optimal sludge hydrolysis conditions a complete solubilisation of the sludge did not occur and 20–30 % of the sludge remained in a suspended form. The extent of solubilisation increased with increasing the concentration of NaOH up to 0.1N. The temperature showed a linear correlation with the extent of the solubilisation and the maximal sludge hydrolysis was achieved at 70 °C. The rate of the solubilisation was the highest during the first half hour and no significant additional digestion was observed after 2 hours of contact period. They conclude that such pre-treatment can efficiently solubilise biosolids in the WAS from pulp-and-paper mills allowing anaerobic digestion to complete in as little as 5–6 days without negatively impacting the biogas production.

The same researchers (Elliott, et al., 2007) stated that the long detention time requirement of the anaerobic WAS digestion has historically deterred its use in the pulp-and-paper industry. They mentioned as a promising reference the tests to reduce the residence time of a sludge generated from the treatment of a synthetic food wastewater. A 4-h detention time using an alkali concentration of 1.8 g/L NaOH at 25, 35, and 55 °C resulted in the COD solubilisation of 28 %, 31 %, and 38 %, respectively. They found alkali pre-treatment to be quite effective at enhancing the anaerobic digestion, as the biogas production was increased by 66 %, 73 %, and 88 % for the pre-treated WAS samples at the temperatures of 25, 35, and 55 °C, respectively. The rate of the biogas production during the first few days of the anaerobic digestion was much higher when the digester received the pre-treated WAS. They argued that the benefit of incubating the WAS under the alkaline conditions was that the small gas bubbles generated due to the anaerobic decomposition floated the WAS which led to the thickening of the sludge, which was beneficial for the subsequent anaerobic digestion.

A beneficial impact of NaOH on protein recovery from a paper-mill WAS was shown by Pervaiz and Sain (2012) who observed a linear increase in protein recovery with increase of the hydroxyl ions. The maximum protein recovery was possible at pH 12, beyond which no improvement in the solubilisation was observed. The maximum recovery of available proteins was achieved at pH 12.0 (24 hour detention time), which was about 32 % more compared to the 2-h treatment at the same pH. A high quantity of the alkali was required to increase the pH from 12 to 12.5, and a 3 to 4 % drop in the protein recovery was observed for the same incremental shift in the pH level. After two further passes through a French press, the maximum cell disruption was observed, showing a 15 % increase in the protein solubilisation compared to the alkali treated control sample. An even better choice was the sonication of the WAS since it yielded 23 % more solubilised protein compared to the alkali-treated control sample. Finally, the maximum protein solubilisation was achieved with the combined effect of the French press and the sonication after the alkali treatment; thereby enhancing the overall protein yield by 44 % compared to alkali treated WAS. The optimization studies thus revealed that the best removal of the intercellular contents from the sludge can be achieved with such combined approach at pH 12 when up to 88 % of available protein was solubilised into the aqueous solution.

The alkaline hydrolysis of a kraft-pulp-mill sludge was studied by Navia et al. (2002). They concluded that for an alkaline pre-treatment with NaOH or KOH, it is possible to obtain an up to 32 % increase in the sCOD/tCOD ratio which could improve the methane yield and the efficiency of the anaerobic digestion process. The initial sCOD/tCOD value of the kraft-pulp-mill sludge was 7.4 % and the maximum values of approx. 32 % were observed for the alkaline reactive doses. There was no significant difference between NaOH and KOH, and 2.4 and 3.4 g/L, respectively, appeared to be the optimum alkaline reactive doses.

Similar hydrolysis conditions were proven to be effective also in some other industrial applications. Uma Rani et al. (2012) found out that at 60 °C with pH 12 the COD solubilisation and the suspended solids reduction of the dairy WAS were 23 % and 22

% higher than that of the control, respectively. The results of the biochemical-methane-potential assay of the pre-treated sludge confirmed that the observed solubilisation led to an increase in the sludge biodegradability since it had nearly 51 % higher biogas production than the control.
For the WAS from a soft-drinks production, according to Vlyssides and Karlis (2004), the COD solubilisation increased significantly with the hydrolysis time at pH ≥ 10 and the temperature ≥ 80 °C, and after 8 h detention time about 80 % of the solubilisation had been achieved. At pH 11 and 90 °C and after 10 h of hydrolysis, the COD concentration was about 69,000 mg/l and the solubilisation rate was still increasing significantly.

Much more work than in the industrial sector was done on the thermo-alkali hydrolysis of the municipal sludge. Some examples confirm our findings with respect to the acidic pre-treatment and to the alkali-temperature synergy. Chen et al. (2007) studied the influence of pH on the performance of the hydrolysis and the acidification of municipal WAS and found out that either acidic pH (pH 4.0, 5.0) or alkaline pH (pH 9.0, 10.0 and 11.0) improved the sCOD concentration. However, the sCOD under alkaline conditions was significantly higher than that at other pH. For 20 days of hydrolysis, they observed 68.3 % sCOD/tCOD at pH 11.0, while it was only 22.1 % at pH 4.0, 13.2 % at pH 7.0, and 13.8% in the control test. In the study done by Feng et al. (2009), the hydrolysis of municipal WAS at pH 10 significantly increased with the SRT increasing from 4 to 16 days, but at a certain SRT the hydrolysis was stable. It increased also with the temperature. At SRT 12 d and pH 10, the average observed concentration of the soluble protein was, respectively, 312.7, 1589.7, 2722.4 and 3050.0 mg COD/L at 10, 20, 30 and 35 °C, and the average soluble carbohydrate concentration was 80.7, 288.6, 384.0 and 418.9 mg COD/L. They concluded that during the WAS digestion, a longer SRT resulted in the dissociation of acidic groups of the extracellular polymeric substances and the repulsions between the negatively charged groups, and more protein and carbohydrate were, therefore, released to the fermentation liquor at the alkaline pH.

Besides NaOH, other alkali reagents were evaluated for the hydrolysis and reported in the literature as well. Su et al. (2013) found out that the alkaline digestion of a municipal WAS with the mixture of NaOH and $Ca(OH)_2$ was advantageous compared to the cases with the sole addition of NaOH or $Ca(OH)_2$. They observed the maximum WAS-solubilisation efficiency in the range of 38–40 % of tCOD. The NaOH to $Ca(OH)_2$ ratios did not exert obvious influence on the WAS solubilisation. They emphasized the advantage that a high VFA production and a good sludge de-waterability can be achieved simultaneously by adding the mixture of NaOH and $Ca(OH)_2$, which could not be achieved by adding NaOH or $Ca(OH)_2$ alone.

Carrère et al. (2010) stated that the alkaline treatment is effective in the WAS solubilisation, with the order of efficacy being NaOH >KOH>$Mg(OH)_2$ and $Ca(OH)_2$. They emphasized that the alkali is normally combined with the thermal treatment. The sludge solubilisation and the anaerobic biodegradability increased with both, the alkali dose and the temperature, to an upper limit. Compared to the thermal hydrolysis alone, the thermo-alkaline-treatment temperature is normally lower, and the increase in temperature normally driven by the chemical processes (from 170 to 120–130 °C). They stated as a drawback the fact that the addition of an alkali increases the mineral content of the digested sludge, which reduces the interest for the co-treatment for the sludge reduction.

The thermo-alkaline hydrolysis is proven to be a good choice for our purpose, although much of the literature pertaining to the alkaline treatment describes how alkali addition enhances as well other sludge disintegration techniques by making the alkali-treated sludge even more amenable to the hydrolysis (Morgan-Sagastume, et al., 2011). In the study done by Doğan and Sanin (2009), it was discovered that the combination of the alkaline and the microwave pre-treatments of municipal WAS led to an improved COD solubilisation. sCOD/tCOD ratio increased from 0.005 (control) to 0.18, 0.27, 0.34 and 0.37 with microwave + pH 10, microwave + pH 11, microwave + pH 12 and microwave + pH 12.5, respectively. Moreover, the DS, VS and COD reductions were improved by approx. 25 %, 35 % and 30 %, respectively. By the use of the combined pre-treatment, the deteriorated de-waterability of the digested sludge due to the alkaline pre-treatment was also improved by 22 % over that of the control.

Sanin et al. (2006) pointed out that the bioflocculation capability of the sludge measured by the quantity of the extracellular polymers and the protein and carbohydrate content of the polymer are to be related to a better flocculation ability as well as an increased hydrophobicity of the floc surfaces. A positive correlation between the cation concentration incorporated into the floc structure and the total extracellular polymeric substances produced has been found out for all cations tested (Ca^{2+}, Mg^{2+} and K^{+}). A lack of improvement and deterioration caused by potassium ions were explained by their inability to form the linkages between extracellular polymeric substances and the floc surfaces due to their monovalent nature. The potassium ions acted as intracellular ions rather than extracellular ions.

In this respect, we noticed that the reduction of the SPH-WAS quantity was accompanied by a decrease of the tDS of the SPH-WAS due to its lower de-waterability. The latter would be a drawback if the SPH-WAS would be given away for the incineration, we however managed to avoid the problems since the recirculation of the SPH-WAS back to the production of the cardboard demands no de-watering as the SPH-WAS is to be added directly to the suspension of the cellulose fibres.

We reported further, from the perspective of the SPH-WAS quantity, that the thermo-alkaline hydrolysis reduced it by 55 %. The portion of the sludge that remained on the belt-press filter was 9.9 mass % for the raw WAS, while only 4.6 mass % for the WAS that was hydrolysed at pH 12, 70 °C. At similar conditions, a 73 % and 40 % reduction of WAS after thermo-alkaline hydrolysis of a municipal WAS was observed by Na et al. (2010) at 60 °C and pH 13 and pH 11, respectively, with an increase in the ratio of sCOD/tCOD. From initial 10 ton/day-sludge generated from the activated sludge process, 2.7 ton/day-sludge through the thermo-alkaline hydrolysis at pH 13 and 60 °C were left. They used as a carbon source for the microorganisms in the aeration tank the intracellular components which were generated by the solubilisation and induced the increase of sCOD.

Instead of the thermo-alkaline hydrolysis, some new pre-treatment techniques for the pulp-and-paper WAS could appear in the future. Baroutian et al. (2013) found out that the wet oxidation of pulp-mill sludge prior to the anaerobic digestion has considerable advantages. Comparing it to the thermal hydrolysis, they found out that both techniques reduced the total solids content of the pulp-mill sludge, but the wet oxidation also destroyed the compounds which would inhibit the methanogenesis and converted them to biologically amenable compounds such as acetic acid.

From the perspective of Količevo Karton, NaOH is however practical to use since it is added regularly to increase the pH of the wastewater above 6.5 before it enters the IC reactor. We can apply it just as well in the hydrolysis reactor with no need for the neutralisation of the LPH-WAS before it is going to be added to the wastewater that enters the IC reactor. Also, the available heat from the steam condensate of the heating boiler exhaust, the thermo-alkaline pre-treatment is our most feasible option.

4.2. Integration of SPH-WAS into cardboard production

4.2.1. Hygienisation of SPH-WAS

We used the synergistic effect of thermo-chemical hydrolysis to solubilise the organics and to reduce and hygienise the WAS. This phenomenon is common for different pre-treatment methods. γ-irradiation, which has been studied mainly for its pasteurization effect, and has been adopted as a disinfectant for wastewater and WAS in western countries, was also reported to release soluble carbohydrates from WAS and was considered as a pre-treatment option for the anaerobic digestion of WAS (Yuan, et al., 2008). An ultrasound treatment kills the pathogenic microorganisms in sludge effectively and the digested sludge is stable and may be disposed of harmlessly (Show, et al., 2010). Also, if the sludge is thermophilically digested, faecal streptococci and faecal coliforms are destroyed and the USEPA standard for Class A Biosolids can be met (Kuo, et al., 2010). Close to our pre-treatment is the treatment with lime, which involves the addition of either CaO or $Ca(OH)_2$ in order to raise the pH to values of 11 or higher to kill off the pathogens (Luste, et al., 2009).

We compared the presence of pathogens, total coliforms, E.coli and enterococci, in SPH-WAS with that in untreated raw WAS, used as a control (Table 11).

Table 11. Results of microbiological tests of WAS.

Test	Raw WAS	SPH-WAS
Total colliforms	positive	negative
E. coli	positive	negative
Enterococi	negative	negative

After our hydrolysis conditions for 2 hours at pH 12 and 70 °C all three indicative microorganisms were below the detection level and the hygienisation process was assured. The LPH-WAS was pathogen-free and can be further considered as a raw material for the production of the cardboard.

4.2.2. SPH-WAS as raw material

According to the findings of the previous section, we saw that the hydrolysis enabled, through its hygienisation, the SPH-WAS to become, from the microbiological point of view, suitable as a raw material for the production of the cardboard. In this section we will use optical and mechanical criteria to further determine the suitability of the SPH-WAS.

Figure 30. Formation of the middle layer of the cardboard with and without 0.5, 1 and 5% addition of SPH-WAS (HR), mixed with fresh fibres (FF).

We are starting from the fact that the annual production of cardboard in Količevo Karton is 200,000 t and the available amount of SPH-WAS is approximately 400 t, annually (from 14 t/h of WAS remains 3.3 % as the filter cake with 9 % DS). This hygienised SPH-WAS could substitute a part of the 100,000 t of raw material that is used annually for the production of the cardboard middle layer (approx. 50% of the cardboard weight). Based on 0.4 % ratio between the SPH-WAS and the middle layer weights and the fact that it would be practically impossible to add SPH-WAS uniformly at this ratio to the cardboard production, a series of cardboard sheets was prepared with and without a higher, up to 5%, addition of SPH-WAS, which resulted from the hydrolysed WAS (Figure 30 and Figure 31).

Figure 31. Formation of the middle layer of the cardboard with and without 0.5, 1 and 5% addition of SPH-WAS (HR), mixed with waste paper fibres (WP).

We proceeded with a stepwise elimination of the possibilities for the use of the SPH-WAS as a raw material for the cardboard. We tested to what extent the common incoming control parameters, divided into the optical and mechanical properties of two groups of standard raw materials (fresh fibres and waste paper) for the production of the cardboard, are influenced by the addition of SPH-WAS.

Considering the optical properties, mesurements of the brightness showed that a 1% addition of the SPH-WAS to the fresh fibres did not deteriorate it, while it decreased notably for a 5% addition of the SPH-WAS (Table 12).

Table 12. Comparison of the brightness of the sheets with different additions of SPH-WAS.

Brightness (%)	SPH-WAS addition to	
SPH-WAS addition	Fresh fibres	Waste paper
0%	60.3 ± 0.4	48.3 ± 0.6
1%	60.1 ± 0.2	48.1 ± 0.2
5%	56.5 ± 0.9	43.7 ± 0.3

A similar conclusion was derived from the measurements of the SPH-WAS additions to the waste paper. The brightness comparison thus limited the addition of the SPH-WAS below the 5% concentration, showing that a 1% mixture is acceptable for both fresh fibres and waste paper, because the corresponding brightness does not decrease below -1 % tolerance minimum with respect to the brightness of the standard raw materials.

The mechanical properties were tested through the strength of the sheets resisting the force acting in longitudinal and vertical directions. The former was expressed in terms of a tensile index. The addition of SPH-WAS to the fresh fibres caused a 12 % decrease in the tensile index for a 1 % addition and a 9 % decrease for a 5 % addition (Table 13).

Table 13. Comparison of the tensile index of sheets with different additions SPH-WAS.

Tensile index (Nm/g)	SPH-WAS addition to	
SPH-WAS addition	Fresh fibres	Waste paper
0%	10.8 ± 0.6	27.5 ± 1.2
1%	9.5 ± 0.2	21.6 ± 1.2
5%	9.8 ± 0.4	21.2 ± 0.2

An even more pronounced decrease caused the SPH-WAS admixture with the waste paper. The tensile index was deteriorated for a substantial 21 and 23 %, for 1 and 5 % additions, respectively. The tensile index comparison limited the use of the SPH-WAS in terms of the stiffness of the cardboard which allows -15 % tolerance minimum with respect to the values of the standard raw materials.

The resistance in the vertical direction was tested in terms of the burst index. It decreased by up to 16% for mixtures of SPH-WAS with fresh fibres (Table 14).

Table 14. Comparison of the burst index of sheets with different additions of SPH-WAS.

Burst index (kPa.m2/g)	SPH-WAS addition to	
SPH-WAS addition	Fresh fibres	Waste paper
0%	0.25 ± 0.07	1.27 ± 0.02
1%	0.21 ± 0.04	1.03 ± 0.05
5%	0.21 ± 0.03	0.96 ± 0.03

The difference is again more visible for the mixture of SPH-WAS and the waste paper. The SPH-WAS decreased the burst index by 19 and 24% for 1 and 5% additions, respectively, which is more than the -15 % tolerance that Količevo Karton allows for its cardboard grades, except for the so-called liner grade where the stiffness is not of such importance.

Besides the microbiological and physical considerations, the chemical considerations have to be included as well. The cardboard from fresh fibres is namely intended for the packaging of food and pharma products, which is under restrictions for extra-high-purity raw materials (RecXXXVI).

From the estetic point of view, SPH-WAS is also better suited for mixing with recovered fibres from the waste paper than with fresh fibres from the wood pulp, because of the higher purity of the latter and the resulting high contrast spots, which are visible in Figure 32.

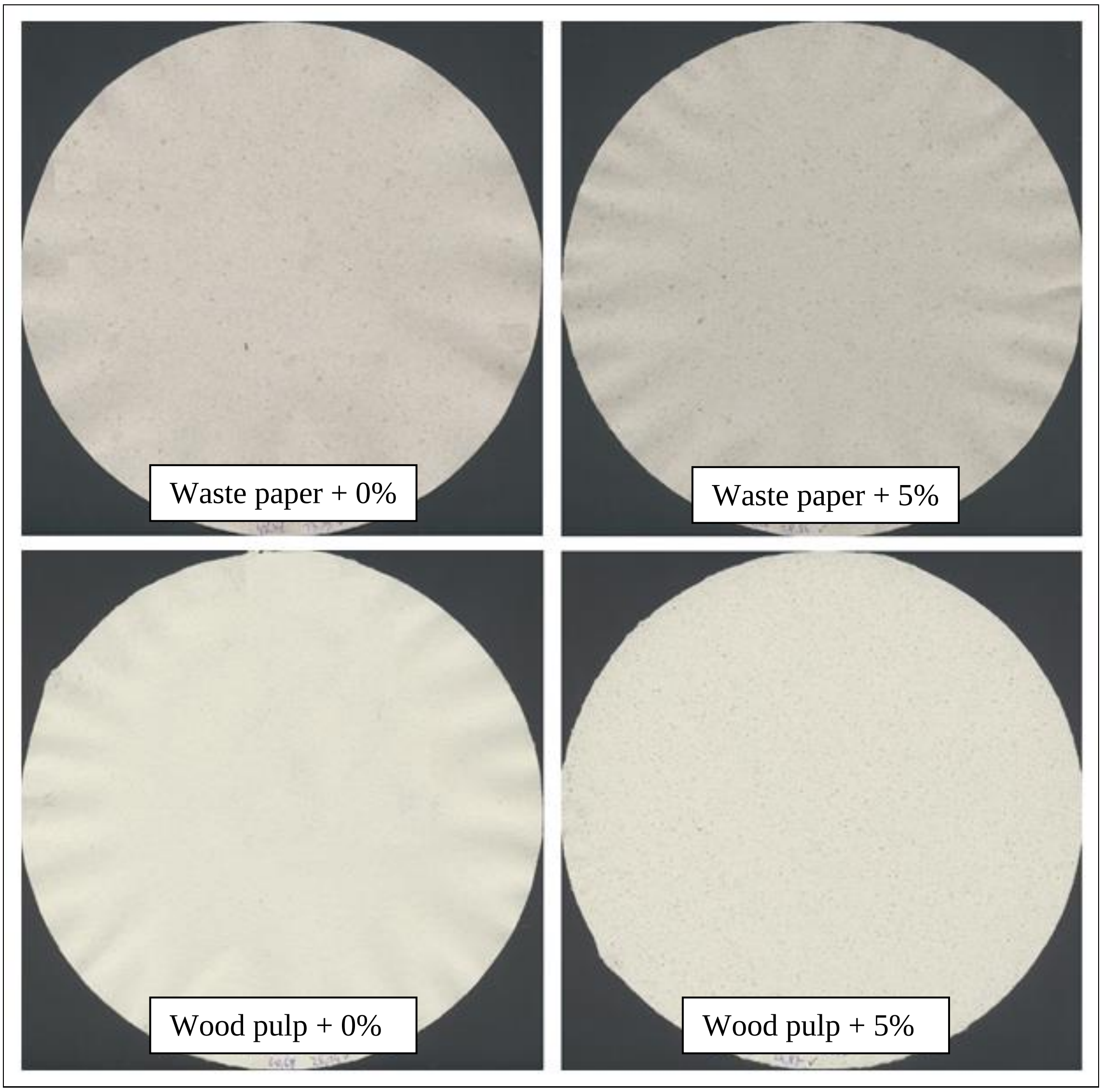


Figure 32. Formation of the middle layer of the cardboard with and without a 5% addition of SPH-WAS, mixed with waste paper (top) and fresh fibres (bottom).

Based on the comparison of the burst index as well as the tensile index, the use of SPH-WAS is best suited to the production of a cardboard grade that does not play the role considering the stiffness of the packaging, for the liner board. Considering the annually available quantity of SPH-WAS (approx. 400 t of dry matter), a 1% addition to the middle layer would demand 40,000 t of middle layer, which represents 50% within the liner board production. This means 40,000 t of liner board annually for an eventual 2% addition, which has to be tested on a large scale. In this respect, it would be possible to use the SPH-WAS during the cardboard production, together with the waste paper, as a raw material.

4.2.3. Discussion

The WAS solubilisation over 90 % and the recirculation of the LPH-WAS as a nutrient to the biological wastewater-treatment plant is an attractive solution if we consider it in terms of the reduction and the re-use of the solid waste. Especially when the latter is at the same time hygienised by the hydrolysis at pH 12 and 70 °C, so that it is suitable as raw material in the cardboard production. The indicative pathogens, total coliforms and E. coli, which were present in the raw WAS were no longer detectable in the hydrolysed WAS at pH 12, 70 °C, for 1 hour.

Similar complete destruction of faecal streptococci reported Lu et al. (2008) concluding that the pre-treatment of a primary municipal sludge at 70 °C completely destructed the faecal streptococci, which they choose as an indicator pathogen in the primary sludge, compared to the process without the pre-treatment that resulted in a partial pathogen-reducing effect. They confirmed in this way the hygienisation effect of the hyperthermophilic (70 °C) pre-treatment step on the thermophilic (55 °C) anaerobic digestion of sludge.

Noticing the drop of the brightness by approximately 5 and 10 %, we further concluded that the addition should be limited below 5 mass % of SPH-WAS dry matter to the fresh and recycled fibres. The brightness was not deteriorated by the 1 % SPH-WAS addition. Since also the tensile index decreased from approximately 10 to 20 % when already 1 % of SPH-WAS was added to the fresh and recycled fibres, respectively, and the burst index decreased by approximately 15 to 20 % for the same samples, we limited the use of the SPH-WAS to the production of the liner cardboard which has lower stiffness demands.

The study of the biological sludge re-use for papermaking by Huber et al. (2013) checked the possibility to recycle a bio-treated sludge directly in the paper manufacturing (as a filler), and to compensate for the loss of mechanical properties by appropriate surface sizing with the help of the starch. When very high mechanical properties were required, they saw no longer any advantage in re-using the bio-sludge. In situations where the bio-sludge re-use was advantageous, they limited the re-use ratio below 2 % otherwise the increase in the drainage resistance was unacceptable for the paper-production process. Additionally, they concluded that the re-using of 2 % of the bio-sludge for the paper manufacturing should not increase the microbiological contamination of a paper sheet significantly. In the present situation, they found the bio-sludge re-use as not cost-efficient. However, this may change in the near future, as the cost of the sludge disposal and the price of the starch may change to more favourable conditions.

In general, new possible applications of the WAS are increasingly examined. To reduce the production cost of polyhydroxyalkanoates and the disposal amount of the excess municipal sludge simultaneously, Mengmeng et al. (2009) tested the feasibility of using the fermentative VFAs as carbon sources to synthesize polyhydroxyalkanoates by the activated sludge. VFAs generated from the excess sludge fermentation were proven to be a suitable carbon source for this purpose. A higher temperature and the alkaline condition were the favourite conditions to enhance the VFAs yield from the excess sludge fermentation. At pH 11.0, 60 °C and fermentative detention time of 7 days, the VFAs yield was satisfactory 258.65 mgTOC/gVSS. A considerable amount of cellular biopolymers and wood fibers in the pulp-and-paper mill WAS convinced Edalatmanesh et al. (2010) that the sludge can be a proper candidate for producing biocomposites. Their results showed that almost 50 % of the sludge consisted of biopolymers associated with wood fibers. They employed the NaOH extraction method in order to isolate and quantify the extracellular polymeric substances and total cellular biopolymers (intra- and extracellular). The addition of NaOH resulted in the ionization of several charged groups, since the isoelectric points in proteins are generally below pH 4–6. Consequently, ionization of proteins caused a strong repulsion between the extracellular polymeric substances within the gel which resulted in a higher water solubility of the compounds. Vaskova et al. (2012) found out that paper mill WAS has great potential to function as a valuable carbon source for fungi growth.

That the minimization of the waste generation from the pulp-and-paper production has the highest priority concluded also Monte et al. (2009). They stated that due to the large quantities of the waste generated, the high moisture content of the waste and the changing composition, the recovery methods, for example, conversion to fuel components, are simply too expensive and their environmental impact uncertain. Stoica et al. (2009) rated the biogas as in general more valuable than sludge as a fuel, and the electricity more valuable as an energy carrier than the biogas and the sludge. They pointed towards the anaerobic digestion of the sludge which enables that the major part of the nutrients can be re-circulated. A prolonged cycle for nutrients within the wastewater-management process reduces the demand for industrially produced nutrients and is preferable from a sustainable development point of view.

Unlike the above mentioned use of an untreated WAS as a raw material for the cardboard production, we are proposing a synergy between the re-use of the SPH-WAS and the LPH-WAS which is a better way of the “zero-sludge”-concept implementation.

4.3. Pilot plant UASB experiment

4.3.1. Anaerobic digestion and biogas production

The purpose of integrating the LPH-WAS into the existing anaerobic treatment of raw wastewater is based on the widespread application of UASB reactors to recover the energy through high-rate AD from either soluble or solid types of wastes (Demirel and Scherer, 2008). In practice, however, not all of the methane potential in the substrates can be extracted in AD within the reactor residence time and it has to be investigated to see whether such integration is feasible.

UASB was first inoculated with anaerobic granules from the UASB reactor of Količevo Karton wastewater-treatment plant in order to adopt micro-organisms and to verify the performance of the pilot UASB reactor. Then it was fed with pulp-and-paper raw wastewater (control experiment) and later in sequence the LPH-WAS was added. We loaded it carefully, starting with a lower dosage and increasing it towards the addition of the whole available quantity (according to the conditions in our model plant of Količevo Karton).

The addition of the LPH-WAS to the raw wastewater was based on the ratio of the amount of WAS relative to the amount of raw wastewater in Količevo Karton (the average on an annual basis is approx. 6%) as well as on its availability through the WWTP’s operation. Therefore, the percentage of added LPH-WAS varied from 0 to 12 %. In practice, it is important to avoid situations involving organic overloads, which could unbalance the process with respect to the acidogenic phase. Therefore, the organic loading rate (OLR) was varied between 2 and 10 kg/m^3/day, simulating the conditions in the Količevo Karton WWTP with a design maximum OLR of 16 kg/m^3/day, which varies considerably on a daily basis, depending on the actual cardboard production (Figure 33). Towards the end of the experiment we heavily overloaded the reactor by increasing the OLR to 35 kg/m^3/day with an average mixture of a 5% LPH-WAS and raw wastewater, and the reactor was still operating. We also operated with a 10 % mixture for 10 consecutive days (day 99 to day 108), which also presented no problems. The effluent pH remained within the limits of 7.0–7.5.

The average SBP with no addition of the LPH-WAS was 0.236±0.056 m^3/kg$_{COD}$ (Figure 34). When adding up to 6 % of LPH-WAS, the SBP decreased to 0.212±0.065 m^3/kg$_{COD}$. Adding more than 6%, up to 12 % of the LPH-WAS, the SBP further decreased to 0.159±0.088 m^3/kg$_{COD}$. These decreases can be attributed to the higher DS concentration. The DS concentrations were 1.697±0.300, 1.866±0.499 and 2.464±0.338 g/kg, respectively, to the raw wastewater, up to 6 % and up to 12 % mixtures of the LPH-WAS in the wastewater. Also, the fluctuations in the SBP were higher when increasing the percentage of the mixture. Although the SBP decreased when adding a higher percentage of the LPH-WAS, the BPR increased from 1.356±0.541 m^3/m^3/day when treating raw wastewater to 1.536±1.198 m^3/m^3/day when treating mixtures of up to 6 % of the LPH-WAS, which is a 13.3 % increase. Adding more than 6 % of the LPH-WAS decreased the BPR to 1.305±0.536 m^3/m^3/day.

The BPR values multiplied by the two corresponding influent CODs give a biogas production increase of 16%. Since at full scale the liquid portion of the WAS and raw wastewater mixture will rarely be more than 6%, the potential for more biogas increases to 20 %.

COD removal is, in addition to biogas production, one of the predominant estimators for the performance of an anaerobic reactor (Figure 35). The tCOD removals were 80.4±10.8 %, 76.5±11.7 % and 70.1±14.6 %, respectively, for the raw wastewater, and up to 6 % and 12 % for the LPH-WAS and raw wastewater mixture. Although the effective biodegradation in our pilot reactor was evidenced by tCOD removal efficiencies that were comparable to the Količevo Karton WWTP, an excessive addition of the LPH-WAS could eventually lead to the accumulation of non-degradable matter and should be avoided. After reviewing the results, we can state that adding up to 6 % of the LPH-WAS to the raw wastewater does not hinder the UASB operation significantly, and it can be feasible. Operating under higher loads of the LPH-WAS and raw wastewater mixture, although at an equal OLR, reduces the efficiency of the anaerobic treatment significantly; however, it is still within the acceptable limits.

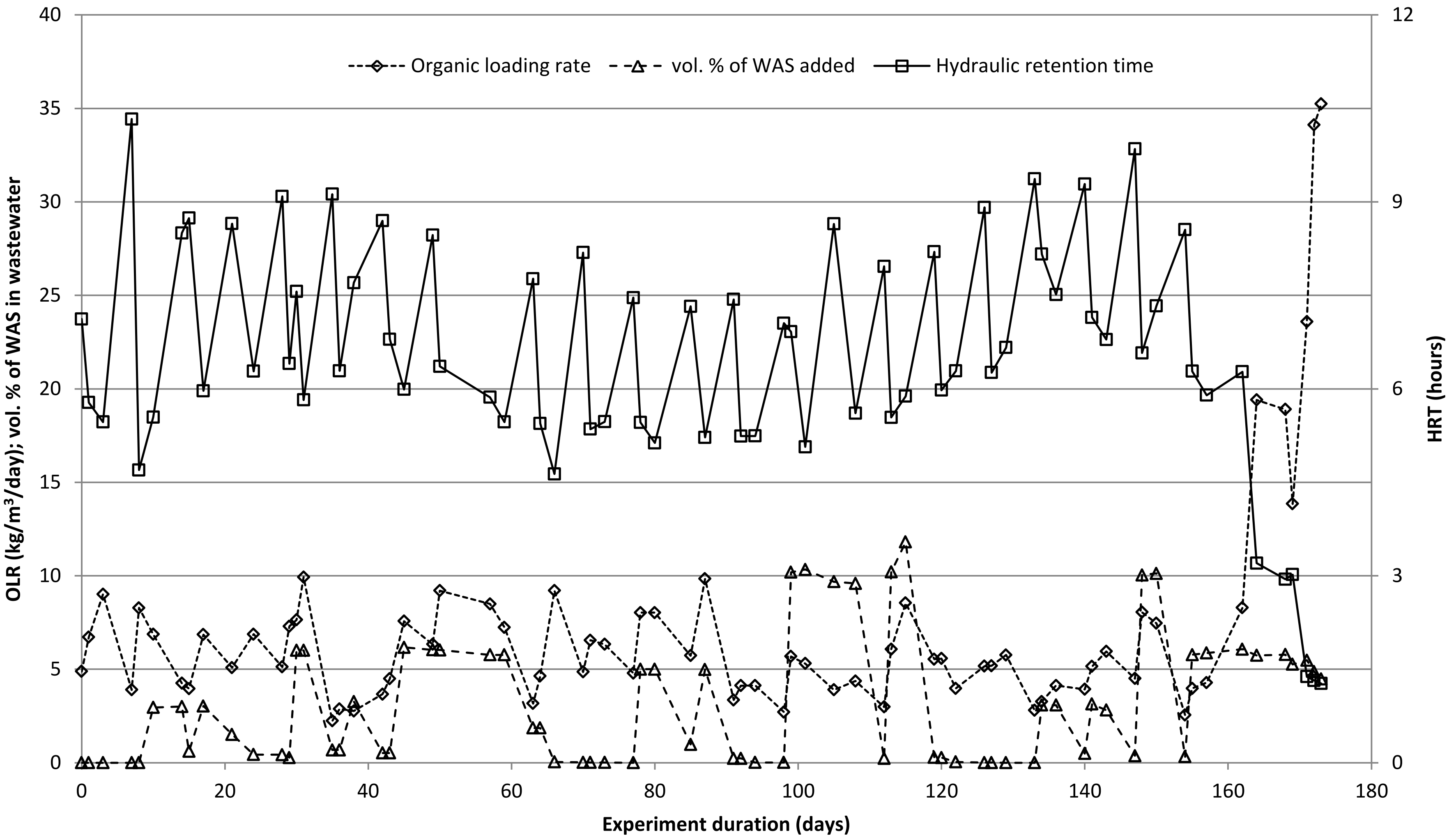


Figure 33. Pilot-plant experiments data; OLR (organic loading rate), volume %. of liquid portion of WAS, HRT (hydraulic retention time).

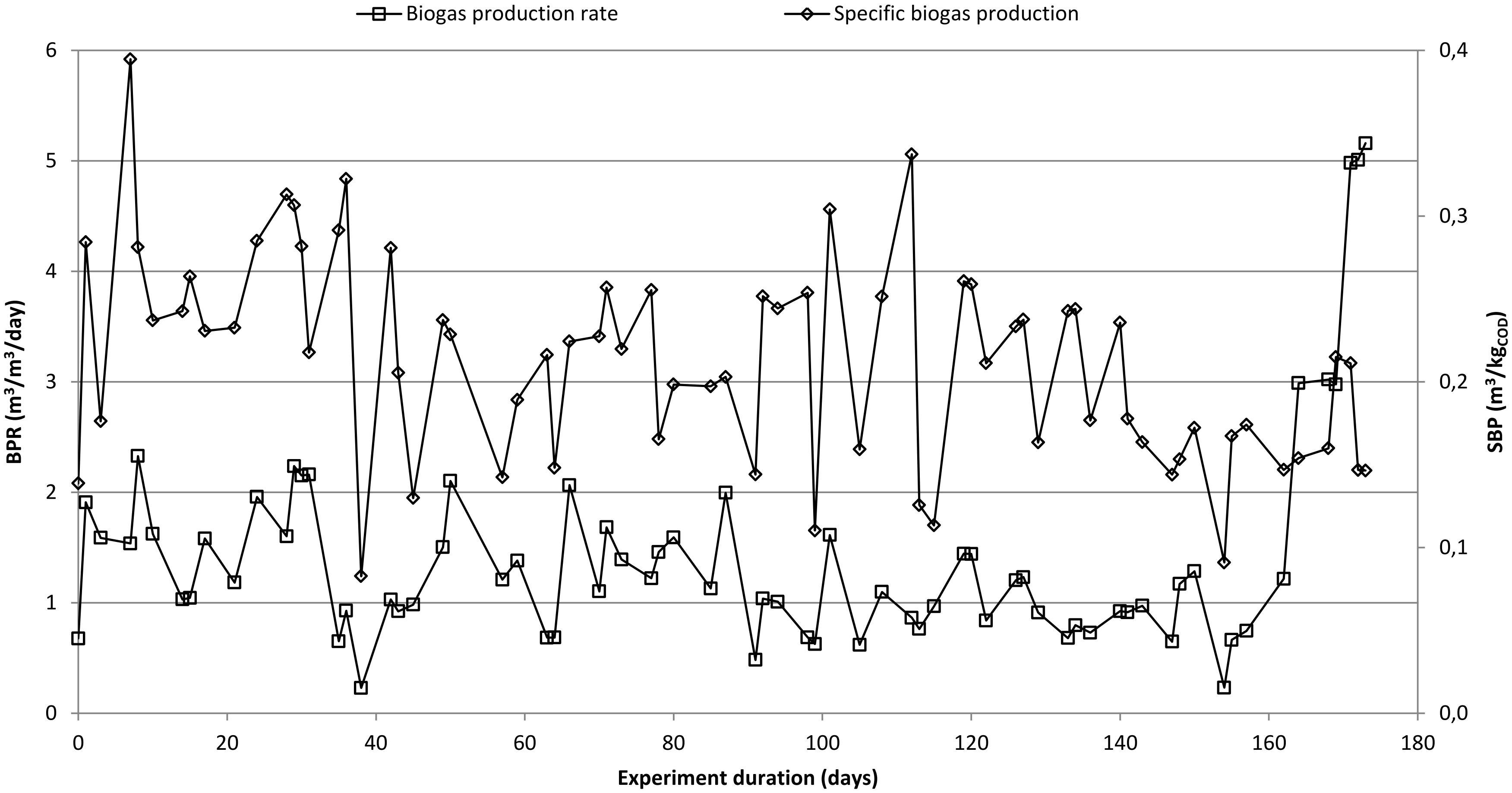


Figure 34. Pilot-plant experiments data; BPR (biogas production rate), SBP (specific biogas production).

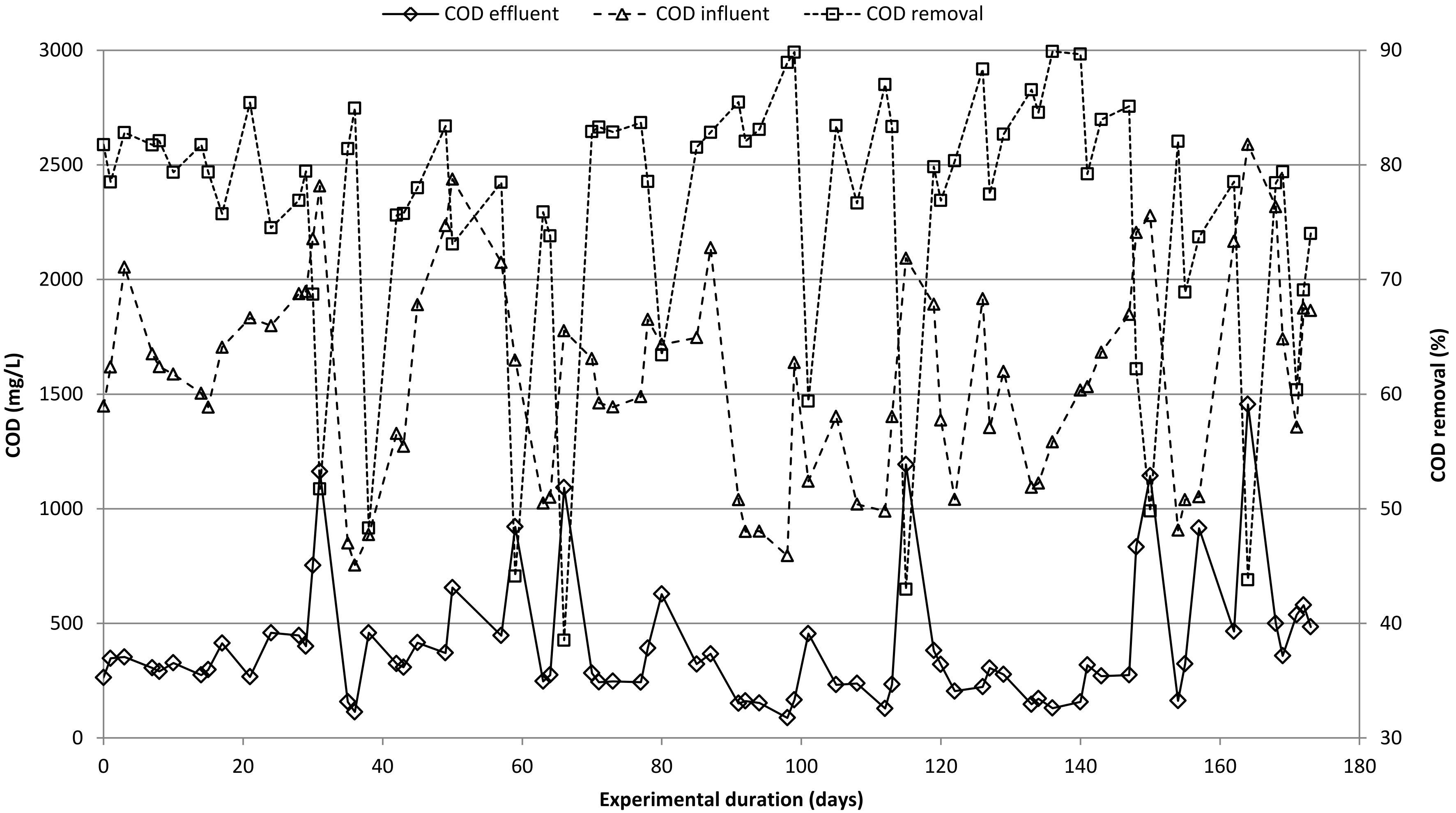


Figure 35. Pilot-plant experiments data; COD removal.

A detail taken from all the measurements, i.e. some characteristic measurements organized according to an increasing addition of LPH-WAS, COD of influent and flux, presented in Table 15Table 15, illustrates the above mentioned trends of decreasing SBP and increasing biogas production.

Table 15. Parameters of biogas production with and without 6 and 10 % additions of LPH-WAS.

LPH-WAS addition	COD in (mg/L)	COD removal (%)	Flow (L/day)	Detention time (h)	Load (kg/m^{3}day)	Biogas (mL/min)	Specific biogas production (m^3/kg$_{COD}$)
6 % addition							
0%	1773 ± 144	88.4	32	8.9	5.16	10.04	0.233
		76.9	32	9.1	5.12	13.35	0.313
		82.9	35	8.2	4.85	9.19	0.227
		79.8	35	8.2	5.54	12.04	0.261
		81.5	39	7.3	5.72	11.27	0.236
		82.7	43	6.7	5.76	10.62	0.228
		79.4	45	6.4	7.30	18.64	0.307
		74.5	46	6.3	6.87	14.88	0.253
		78.5	50	5.8	6.72	15.92	0.284
		82.1	61	4.7	8.28	19.40	0.281
							0.26±0.03
	1924 ± 54	88.4	32	8.9	5.16	10.04	0.233
		76.9	32	9.1	5.12	13.35	0.313
		79.8	35	8.2	5.54	12.04	0.261
		79.4	45	6.4	7.30	18.64	0.307
							0.28±0.04
6%	2235 ±15	83.4	34	8.5	6.33	13.90	0.263
	2423 ± 21	68.7	38	7.6	7.64	17.94	0.282
			45	6.4		16.69	0.221
		73.1	45	6.4	9.20	17.53	0.229
		51.7	49	5.8	9.93	18.33	0.222
							0.24±0.03
12 % addition							
0%	963 ± 94	86.6	31	9.4	2.80	5.67	0.243
		81.4	32	9.1	2.24	5.43	0.291
		87.0	36	8.0	2.98	6.64	0.311
		85.5	39	7.4	3.36	8.99	0.321
		82.1	55	5.2	4.12	8.65	0.252
		83.1	55	5.2	4.13	8.45	0.245
							0.28±0.03
	1240	86.6	31	9.4	2.80	5.67	0.243

LPH-WAS addition	COD in (mg/L)	COD removal (%)	Flow (L/day)	Detention time (h)	Load (kg/m^{3}day)	Biogas (mL/min)	Specific biogas production (m^3/kg$_{COD}$)
	± 161	75.6	33	8.7	3.67	7.87	0.258
		85.5	39	7.4	3.36	8.99	0.321
		77.5	46	6.3	5.19	10.27	0.238
		76.9	48	6.0	5.57	12.01	0.259
							0.26±0.03
	1416 ± 60	89.7	31	9.3	3.92	8.70	0.266
		75.6	33	8.7	3.67	7.87	0.258
		79.4	33	8.7	3.96	8.70	0.264
		83.7	39	7.5	4.79	10.19	0.255
		81.8	40	7.1	4.88	12.49	0.307
		77.5	46	6.3	5.19	10.27	0.238
		76.9	48	6.0	5.57	12.01	0.259
		83.3	54	5.4	6.55	14.03	0.257
							0.26±0.02
12%	1842 ± 38	83.4	33	8.6	3.89	7.098	0.219
		76.7	51	5.6	4.37	8.569	0.248
		59.4	57	5.1	5.30	12.311	0.279
							0.25±0.03
	2093 ±10	43.0	49	5.9	8.54	9.853	0.138
	2242 ±52	62.2	44	6.6	8.05	9.973	0.157
		49.8	39	7.3	7.46	9.828	0.158
							0.16±0.01
Overloading							
0%	1734 ± 73	82.9	35	8.2	4.85	9.19	0.227
		81.5	39	7.3	5.72	11.27	0.236
		74.5	46	6.3	6.87	14.88	0.253
							0.24±0.01
5%	2283 ± 127	83.4	34	8.5	6.33	12.52	0.237
		73.1	45	6.4	9.20	15.96	0.208
		82.8	55	5.2	9.83	16.63	0.203
		79.4	95	3.0	13.85	25.19	0.218
		78.4	98	2.9	18.90	27.51	0.190
		60.4	209	1.4	23.59	40.81	0.208
							0.21±0.02

Taking into consideration the less-homogenous nature of the LPH-WAS with respect to the raw wastewater, the operating parameters were satisfactory. In fact the WAS solubilisation of over 90% and the recirculation of its liquid portion as a carbon source to the influent of the anaerobic WWTP is an attractive solution if we consider it in terms of the reduction of a solid waste as well. This is particularly the case when the latter is at the same time hygienised by the hydrolysis at pH 12 and 70 °C, so that it is suitable as a raw material in the production of cardboard, which gives the pulp-and-paper industry the possibility of implementing the "zero-sludge" concept.

4.3.2. *Discussion*

We mixed different additions of the LPH-WAS up to 6 % and up to 12 % into the control substrate, which was the raw wastewater from Količevo Karton cardboard production. Due to a lower homogeneity of the mixture of the raw wastewater and the LPH-WAS with respect to the raw wastewater, the SBP decreased on average from 0.24 to 0.21 $m^3/kg_{COD,}$ while the efficiency of the COD removal decreased from 80 % to 76 % for the most applicable combination of HRT of 3-5 hours and the LPH-WAS addition of 6 %. The BPR increased from 1.356±0.541 m^3/m^3/day when treating the raw wastewater to 1.536±1.198 m^3/m^3/day when treating the mixtures of up to 6 % of the LPH-WAS, which is a 13.3 % increase.

At a much longer HRT, Balasubramanian and Muthukumar (2012) found out the COD removal of 92 % at the optimum HRT 10 h, with a gas yield of 3.2 m^3/m^3/day and a methane production rate of 0.29 m^3/kg COD removed, when they treated a pulp-and-paper mill wastewater in a hybrid UASB with effective microorganisms. Without the use of effective microorganisms, the maximum effluent COD removal was 83 % at a HRT of 12 hours with a gas production of 1.162 m^3/m^3/day and a methane production rate of 0.28 m^3/kg COD removed.

sCOD and VS removal efficiencies were improved by Yunqin et al. (2010) from 56 to 71 % and from 33 to 44 %, respectively, with a bio-pre-treatment of a pulp-and-paper WAS. They used an active mushroom-compost extracts prior to the anaerobic digestion at the detention time of 42 days at 37 °C, increasing the methane productivity by 34 % with a peak value of 0.23 m^3/kg VS added at a lower cost compared with other pre-treatments.

When studying the thermo-alkaline pre-treatment of a pulp-mill WAS which is similar to our paper-mill WAS, Wood et al. (2009), found out that the thermo-alkaline pre-treatment at pH 12 and 140 °C can significantly increase both the extent and the rate of the anaerobic bioconversion of the sludge to the biogas. They reported that the biogas production from the untreated sludge was 0.045 m^3/kg of inserted COD and 0.20 m^3/kg COD for a kraft-pulp sludge and a sulphite-pulp sludge, respectively. The thermo-alkaline pre-treatment had a higher impact on the biogas yield from the kraft-pulp sludge than from the sulphite-pulp sludge, it increased the total biogas yield to 0.17 and 0.23 m^3/kg COD, respectively. The fraction of sCOD increased for more than 6 times and nearly 60 times after the thermo-alkaline pre-treatment for the sulphite- and the kraft-pulp sludge, respectively. In comparison to the thermal pre-treatment at 170 °C, they found out that the thermo-alkaline pre-treatment resulted in a higher concentration of solubilised COD, protein and carbohydrate, but the biogas yield was only 50 % of the predicted yield. They supposed that the thermo-alkaline pre-treatment solubilised biologically recalcitrant compounds or that this pre-treatment generated inhibitory compounds. The former explanation was chosen as more likely since the thermo-alkaline pre-treatment did not reduce the rate of the biogas production. The findings implied that the solubilised fraction of the pre-treated secondary sludge could be used as a feedstock for the high-rate anaerobic bioconversion at pulp-mill installations.

For a combined alkaline and ultrasound pre-treatment of a WAS from a paper mill, Park et al. (2012), observed that the pre-treatment increased VS removal in the non-thickened (25 g/kg DS) and in the thickened (65 g/kg DS) WAS, by 9 % and 4 %, respectively. The pre-treatment did not increase the overall methane yield, but did increase the initial rate of the methane production. 80 % of total methane/biogas production was reached 5.5-6.5 days faster when pre-treated.

While the development of high-tower reactor systems (especially IC) enabled treatment of dilute effluents and is very suitable for the applications in in-line integrated treatment plants (Habets, et al., 2007), the in-line anaerobic degradation of concentrated effluents presents a challenge. We can state that adding the LPH-WAS up to 6 % to the raw wastewater does not hinder the UASB operation and is feasible.

4.4. Design of hydrolysis reactor

Our next purpose was to determine the dimensions and the regime of operation of the hydrolysis reactor. It functions at 70°C and has to last for at least 120 minutes. The required 70 °C in the reactor will be achieved by co-heating of the WAS with the help of a heat exchanger. The WAS inside the reactor will be homogenised with a stirrer.

We considered as starting conditions the data about the quantity of WAS and the quantity of the raw wastewater. The amount of WAS was 14 m^3/h and the amount of the raw wastewater was 290 m^3/h. In Figure 36 the data of the flux of the WAS to the belt press in Količevo Karton is shown. Within the period from 5.1.2012 to 5.9.2012, 84100 m^3 of WAS was produced, which means an average flux of 14 m^3/h. The ratio of WAS to raw wastewater is then approximately 5%. We determined that one batch has to last 4 hours. We decided for a construction from two equal-sized reactors.

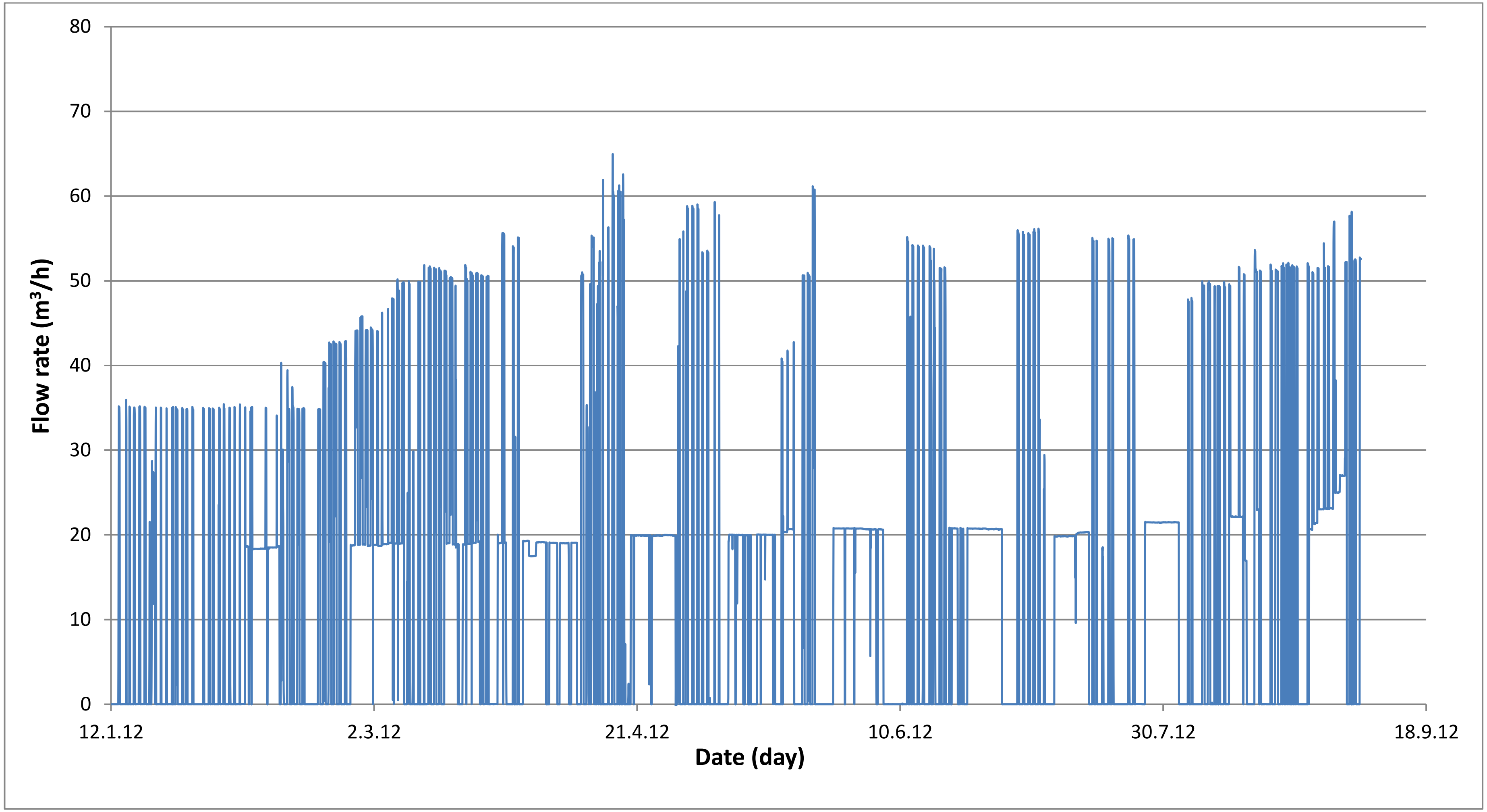


Figure 36. The flux of WAS to the belt press.

We decided that one batch for a duration of 240 minutes (4 h) will operate in the following steps:

1. Loading and heating of WAS to 70 °C for 45 min
2. Operation at 70 °C for 120 min
3. Sedimentation for 45 min (mixing stopped)
4. Releasing the WAS for 30 min (mixing stopped)

The dimensions of the reactor were determined on the basis of an average daily flux of WAS and the time of operation of one batch. We determined that the reactor´s capacity has to be 56 m^3, which is enough for 4 hour batches. We decided for two consecutive reactors with a capacity of 56 m^3, altogether 112 m^3, in order to have some additional capacity and safety. The reactor will be composed of two parts: an upper cylindrical part with a volume of 53.3 m^3 and a lower part which will have conical shape and will serve as a sedimentator with a volume of 10.9 m^3. The total volume will be 64.2 m^3. Figure 37 shows the total height of the active part of the reactor is 5.664 m.

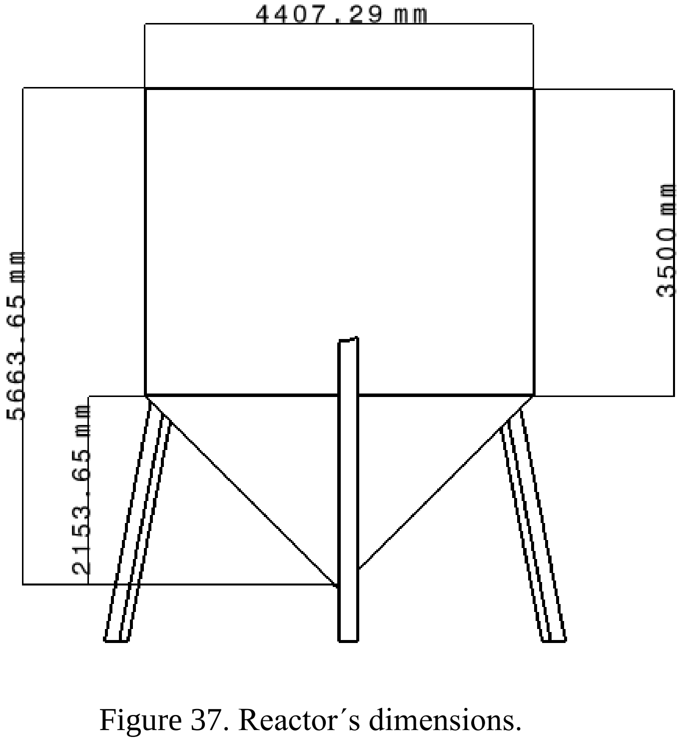


Figure 37. Reactor´s dimensions.

Figure 38 shows the proposed positions for the releasing valves. The distance between them is 0.575 m and 0.645 m. Such a separation between two releasing valves means a quantity of 8.7 m^3 and 10.9 m^3 for the WAS, as shown in Table 16. A release valve for the sedimented SPH-WAS will be located on the bottom of the sedimentator.

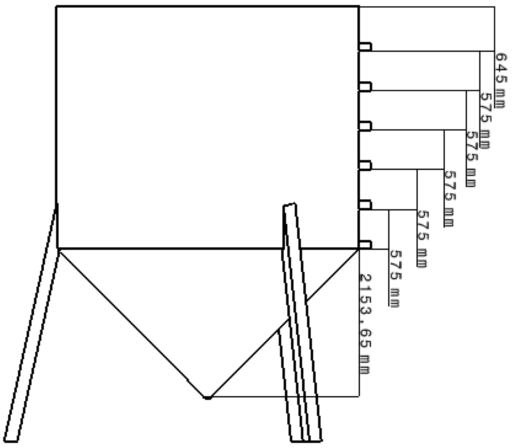


Figure 38. Position of release valves.

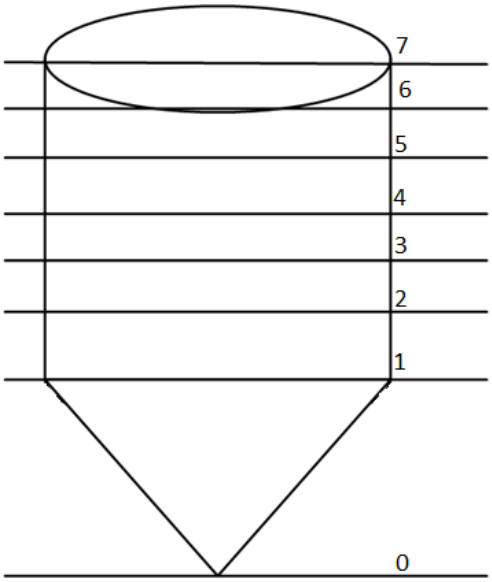


Figure 39. The hydrolysis reactor with the zones for the release of the WAS.

Table 16. The volumes in the reactor between the individual release valves (active volume).

Zone	Volume (m^3)	%
0-1	10.9	17.0
1-2	8.7	13.55

Zone	Volume (m^3)	%
2-3	8.7	13.55
3-4	8.7	13.55
4-5	8.7	13.55
5-6	8.7	13.55
6-7	9.8	15.26
SUM	64.2	

Figure 39 shows the zones for releasing of the WAS. In Table 16, we can see the volumes of the individual zones and the corresponding percentages of the total reactor volume.

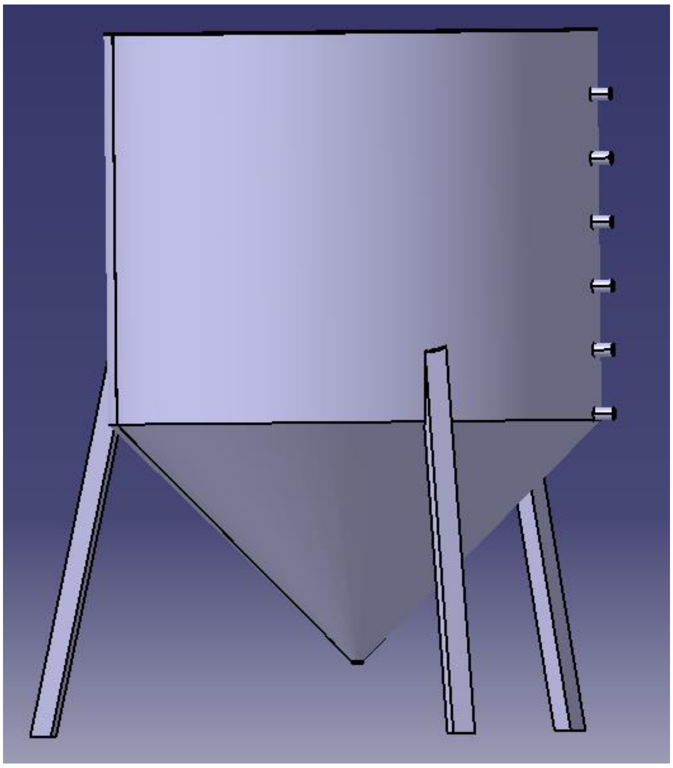


Figure 40. The model of reactor made in the Catia programming tool.

Before it enters the wastewater-treatment plant, the raw wastewater and the LPH-WAS are mixed. The quantities of the LPH-WAS and the raw wastewater are 45 m^3 and 1160 m^3, respectively. After mixing of the LPH-WAS, which has 70 °C, with the raw wastewater, the temperature of which is daily changing, its temperature increases on average by 1.4 °C, i.e., 4.2 %. The maximum raw-wastewater-temperature change reaches 1.7 °C and the minimum is 1.2 °C. Figure 41 shows the data for the raw-wastewater temperature before and after mixing with the LPH-WAS.

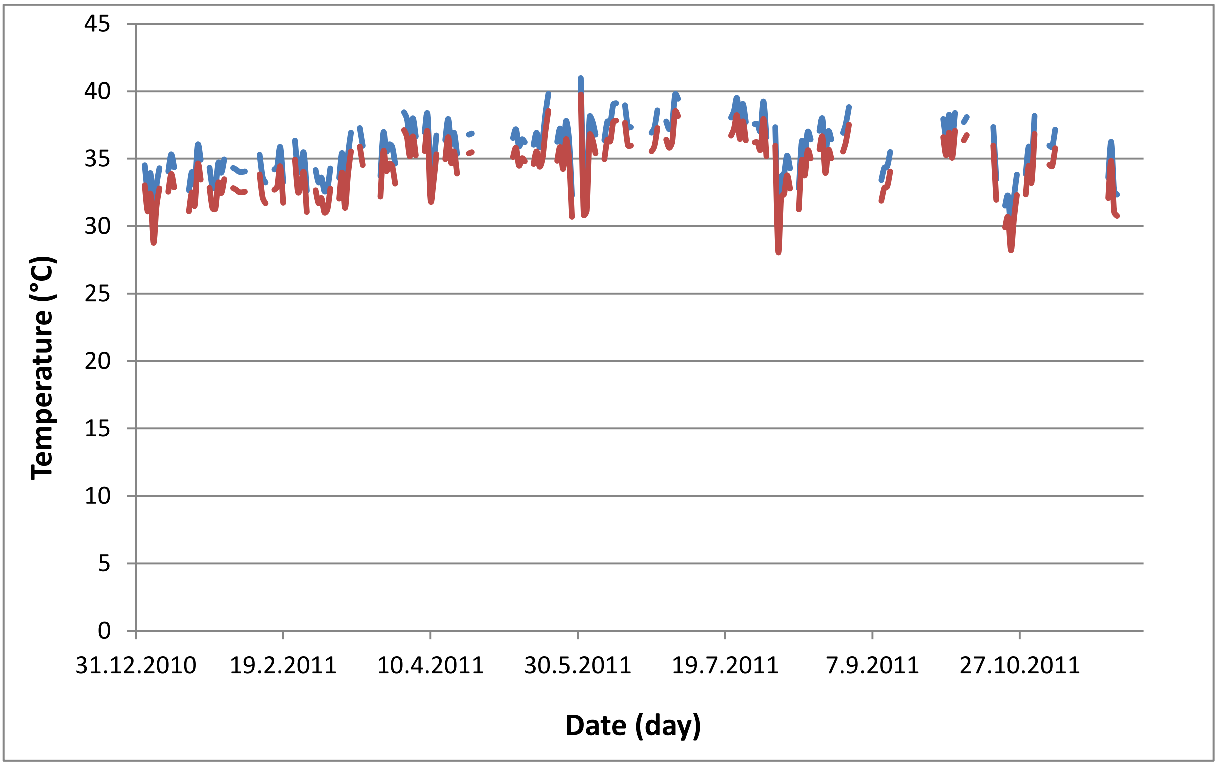
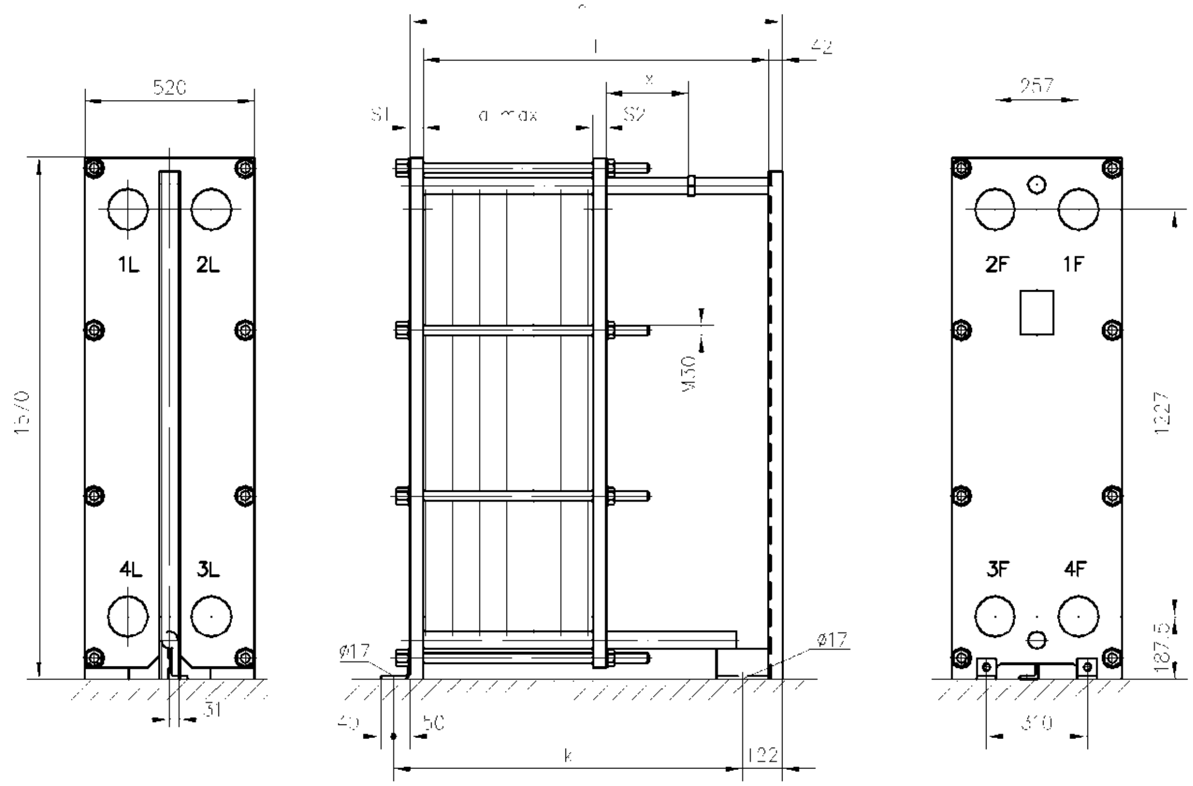


Figure 41. Temperature of the raw wastewater before (red curve) and after (blue curve) mixing with the LPH-WAS. Average temperature change is 1.4 °C.

The WAS has an initial temperature 20 °C and it needs to be heated to at least 70 °C. The heating will be realized with the help of a plate heat-exchanger. The heating medium will be the condensate of the Količevo Karton heating boiler exhaust, with a temperature of 89 °C. Its quantity is 39 m^3/h, while the quantity of the WAS is 14 m^3/h. The appropriate heat-exchanger is commercially available from the company IPROS d.o.o. The heat-exchanger will heat up the WAS to 70 °C by cooling the condensate to 72.2 °C. Figure 42 shows the dimensions of the heat-exchanger.



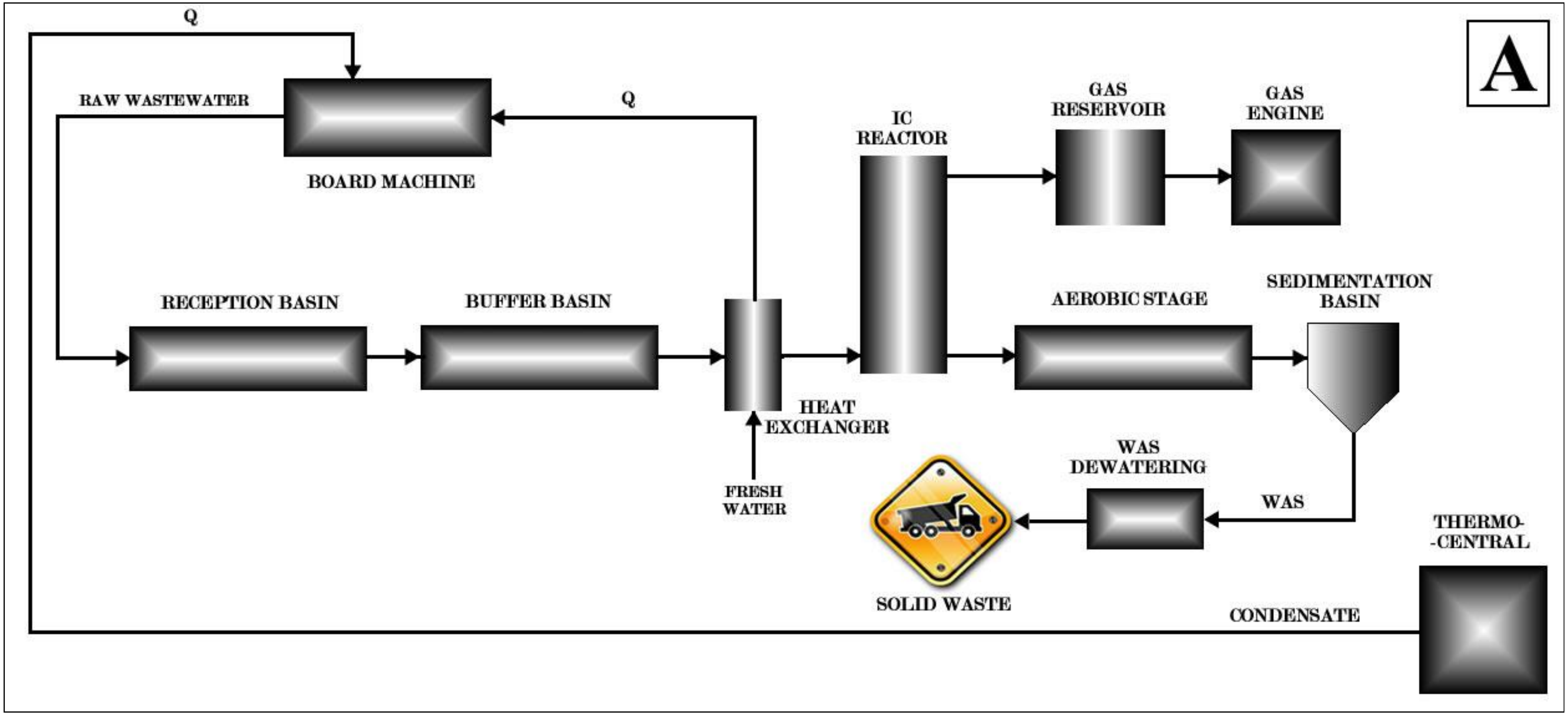
n:	1297 mm	s_1:	40,00 mm	a-max frame:	700 mm	empty weight:	868 kg
k:	1225 mm	s_2:	40,00 mm	a-max actual:	414 mm	max. total weight:	1030 kg
l:	1215 mm			x:	208 mm		

Po	**Size**	**Type**	**Media**	**In**	**Ou**	**Add**	**m**
1F	DN10	Rubber insert DIN 2633 EPDM	Water	x	-	-	4 mm
2F	DN10	Rubber insert DIN 2633 EPDM	Saccharose 45,0	-	x	-	4 mm
2L	DN10	Rubber insert DIN 2633 EPDM	Saccharose 45,0	x	-	-	4 mm
4L	DN10	Rubber insert DIN 2633 EPDM	Water	-	x	-	4 mm

Figure 42. The dimensions of the heat-exchanger.

The heating of the WAS does not represent a problem if we run the condensate through a commercially available heat-exchanger.

The higher temperature of the LPH-WAS causes, during the mixing with the raw wastewater before they enter the anaerobic reactor, an increase in the raw wastewater temperature by an average of 1.4 °C, which represents no problem for the installed wastewater system since the raw wastewater is being cooled in a heat-exchanger before it enters the IC reactor (Figure 43). The cooling medium in this case is the technological water, which takes the extra heat to the cardboard production, which the saves some energy needed for its subsequent heating.


A
Q
RAW WASTEWATER
Q
BOARD MACHINE
IC REACTOR
GAS RESERVOIR
GAS ENGINE
RECEPTION BASIN
BUFFER BASIN
AEROBIC STAGE
SEDIMENTATION BASIN
HEAT EXCHANGER
FRESH WATER
WAS DEWATERING
WAS
SOLID WASTE
THERMO-CENTRAL
CONDENSATE

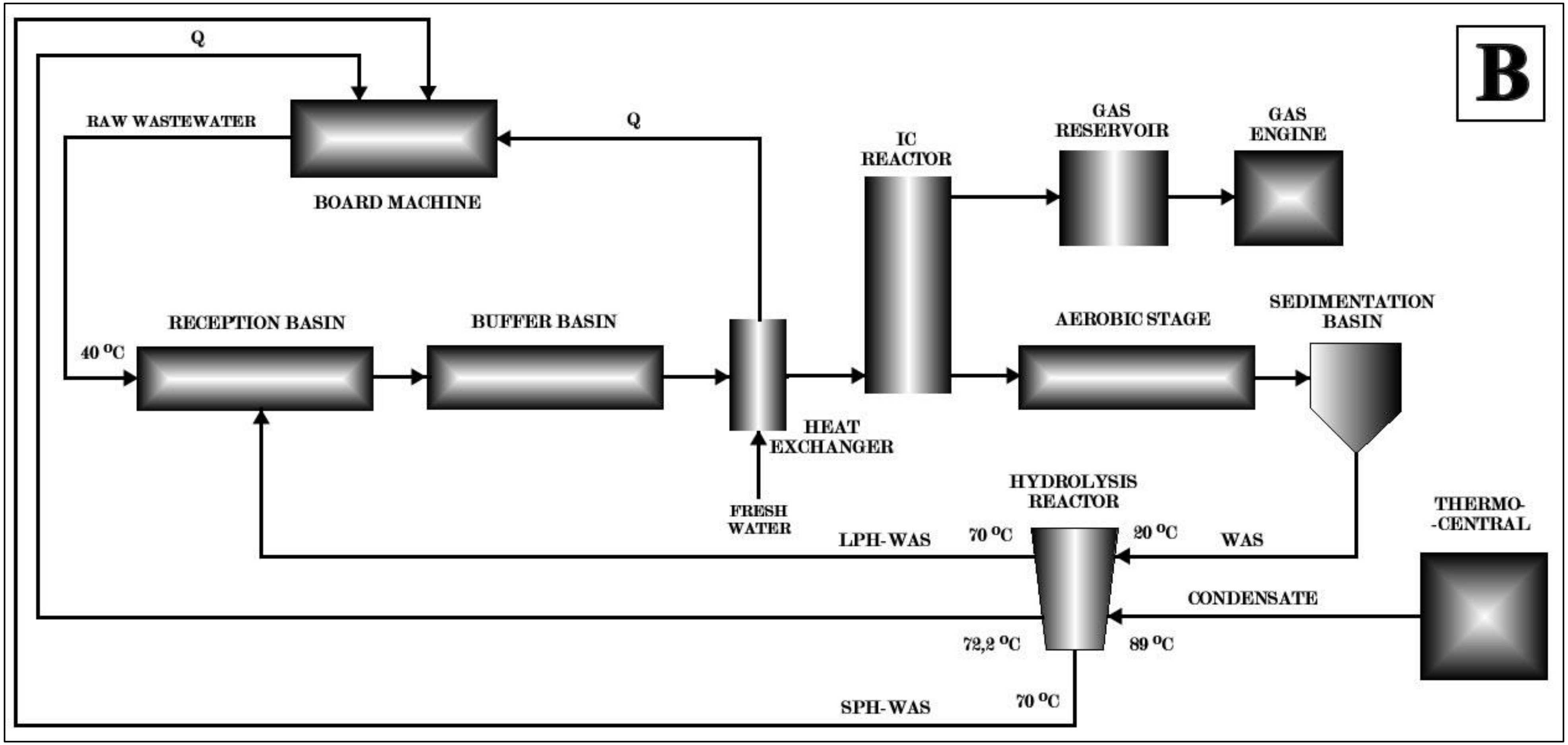


Figure 43. The integration of the hydrolysis reactor into the existing system: before (A) and after (B) situations.

4.5. The impact of the presented results

The decision on the ‘best practicable environmental option’ for treating WAS should be considered on the basis of four categories: technical reliability, cost, environmental sustainability and environmental nuisance. Anaerobic digestion is in this respect a robust technology that reduces solid waste and produces green energy in the form of biogas at the same time. This biogas can be either upgraded to allow it to be directly used as a transport fuel or injected into the gas grid, or it can be de-sulphurised, dried and utilised in CHP systems to provide the wastewater-treatment plant with electricity and heat or be exported in the case of excess. Since this energy is from a renewable source, it also has the added benefit of attracting incentives for the energy producer (Devlin, et al., 2011).

The potential is therefore large for an industry like pulp-and-paper production that treats huge amounts of raw wastewater (2,500,000 m^3 annually in Količevo Karton) with anaerobic digestion and at the end of the day accumulates huge amounts of solid organic waste (3500 t annually). The missing link in the chain, which is the pre-treatment of the WAS, can enhance and consequently enable its digestion within an existing anaerobic reactor and requires a minimal capital investment in comparison with, e.g., anaerobic digestion itself (Roš, et al., 2003).

The results of the present study have shown a high level of solubilisation of WAS (sCOD/tCOD > 0.90) and high biodegradability of the LPH-WAS (70-80% removed COD).

The consequence of the high solubilisation of the WAS is the possibility of complete recirculation of the sludge fractions into the cardboard production and to the IC reactor instead of necessity to remove it as solid waste. On one side, this means at 92 €/t and approximately 3500 t of solid waste (20-25% DS) an annual saving on the level of €320,000. On the other hand, the usage of a reduced quantity of SPH-WAS which is hygienised by the hydrolysis would at approximately 400 t annually (dry matter) mean a saving of €52,000 through the replacement of waste paper as the raw material for the cardboard production with a price of 130 €/t.

The consequence of high enough biodegradability of the LPH-WAS is a potential increase of the biogas production by at least 20%, as follows out from changes of specific biogas production, the influent COD and influent flow and from the available annual quantity of LPH-WAS, which represents 5% of the raw wastewater quantity. An increase of the present incentive (approx. €220,000) for the green electricity for equal percentage would bring an additional €44,000 per year. For further biogas enhancement, some more WAS could be removed from the aerobic system, lowering its concentration and age. The hydrolysis reactor offers also the possibility for the dosing of other organic waste materials and chemicals (e.g., glycerol, methanol).

The above stated benefits support the hydrolysis of WAS as a promising innovation, which was as such applied for patenting under patent number P-201300134.

5. CONCLUSIONS

This PhD thesis presents a procedure for the re-use of aerobic WAS from the pulp-and-paper industry. It is a sustainable alternative to the current method for WAS disposal via incineration.

Our first hypothesis was that it is possible to achieve with the help of the thermo-chemical hydrolysis of the WAS at least a 60-%-dissolution of tCOD which results in high enough percentage of organic matter in LPH-WAS and low enough percentage of organic matter in SPH-WAS. Various combinations of pH, temperature and time, as the main factors of the hydrolysis, were tested. WAS from the biological wastewater-treatment plant of the cardboard producer Količevo Karton was hydrolysed at two extreme pH values, i.e., 2 and 12, in the temperature range from room temperature to 200 °C for an hour to several days. pH 12 was more efficient than pH 2, according to the level of dissolved organic material expressed as the ratio sCOD/tCOD. It reached over 0.9 after just 1 hour of hydrolysis at 70 °C, which proved to be the most suitable temperature. At higher temperatures, the solubilisation of WAS did not even retain such a high sCOD/tCOD, but dropped consistently to 0.8 at 200 °C. The results of the first phase of our research showed that the thermo-chemical hydrolysis of WAS from cardboard production can be effectively achieved. Our first hypothesis was in this way confirmed.

Next, the optimal hydrolysis conditions of pH 12, 70 °C and 1 hour, showing how the concentration of the WAS suspension affects its solubilisation, were optimised. The WAS was concentrated with the help of gravitational sedimentation or centrifugation from normal 25 to 29 and 42 g/l of DS, respectively. The intermediate concentration had a positive effect of enhancing the solubilisation from 0.9 to 0.94, while for the concentrated WAS it lowers the solubilisation effect to 0.8. This shows that a gravitational sedimentator would be a good choice between the wastewater-treatment plant and the hydrolysis reactor.

From the perspective of SPH-WAS, the mass balance showed that the hydrolysis reduced its quantity by 55%. The portion of the sludge that remained on the belt-press filter was 9.9 mass % for raw WAS, while only 4.6 mass % for the WAS that was hydrolysed at pH 12, 70 °C. It is true, however, that the DS of the SPH-WAS decreased due to its lower de-waterability. The latter would be a drawback if the SPH-WAS would be given away for incineration.

In our second hypothesis, we claimed that the SPH-WAS is suitable as the raw material for the cardboard production. The recirculation of the SPH-WAS back to the production of the cardboard, on the other hand, demands no dewatering since the SPH-WAS is to be added to the suspension of cellulose fibres. Next, the pulp characteristics were tested. The criterion of the microbiological, optical and mechanical suitability was applied. The indicative pathogens, total coliforms and E. coli, which were present in raw WAS were no longer detectable in the hydrolysed WAS at pH 12, 70 °C, for 1 hour. The drop of the brightness by approximately 5 and 10 % showed that the addition of 5 mass % of SPH-WAS dry matter to the fresh and recycled fibres, respectively, is too high. The brightness was not deteriorated by a 1 % SPH-WAS addition. The mechanical properties were tested through the strength of the cardboard sheets resisting the force acting in the longitudinal (tensile) and vertical (burst) directions. The former decreased from approximately 10 to 20 % when already 1 % of SPH-WAS was added to the fresh and recycled fibres, respectively. The latter decreased by approximately 15 to 20 % for the same samples. Based on a comparison of the tensile index as well as burst index, the use of SPH-WAS has to be limited to the production of a cardboard grade that does not play a role involving the stiffness of the packaging, to the so-called liner board. Considering the available quantity of SPH-WAS (approx. 400 t dry matter), a 1% addition to the middle layer would demand 40,000 t of middle layer, which represents 50% within the liner board production. The second stage of our research thus proved that it is possible to obtain zero emission of WAS in the production of the cardboard. Thermo-alkali hydrolysis at the same time solubilised a great part of the WAS and hygienised its SPH-WAS. The latter enables the usage of SPH-WAS as a raw material for the cardboard production, while the former makes possible the production of renewable energy from the hydrolysis supernatant. Our second hypothesis was thus confirmed.

Our third hypothesis was that the LPH-WAS can be anaerobically digested in the UASB reactor. The possibility of recycling the LPH-WAS was tested in a pilot anaerobic reactor. We mixed different additions up to 6% and up to 12% – into the control substrate, which was the raw wastewater from Količevo Karton. Due to lower homogeneity of the mixture of raw wastewater and the LPH-WAS with respect to the raw wastewater, the specific biogas production decreased with 6% addition on average from 0.24 to 0.21 $m^3/kg_{COD,}$ while the efficiency of the COD removal remained at approximately 80% for the most applicable combination of HRT of 3-5 hours and LPH-WAS addition of 6 %. The maximum biogas production increase was from 12.5 to 27.5 mL/min, because of the increased organic loading rate. These values guarantee a high level of wastewater treatment and high biogas production. The operating indicators were satisfactory since the actual biogas quantity is increased by up to 20%, because the LPH-WAS increased the influent's COD more than it decreased the specific biogas production. Our third hypothesis was confirmed although the biodegradability of the LPH-WAS was somewhat lower with respect to that of the raw wastewater.

Our forth hypothesis was that it is possible to integrate the hydrolysis reactor together with the heat regeneration system in a sustainable way into the existing system of the cardboard production. This hypothesis was confirmed apart from the assumption that a heat regeneration system will be needed. The possibility to use the condensate of the heating boiler exhaust as the heating medium for the WAS in the hydrolysis reactor and the fresh water for the cardboard production as the cooling medium for the LPH-WAS, caused the change of our plan since the heat regeneration was no longer needed. Nevertheless, the forth hypothesis can be considered as confirmed.

Based on above findings, we constructed a large-scale hydrolysis reactor as a sustainable solution for the problem of providing for a significant amount of WAS as a solid waste and as a source of a new nutrient to enhance the anaerobic production of methane and electricity from such a renevable source, as well as a source of a raw material for the cardboard production.

Our objective to introduce the “zero-sludge” concept into the cardboard production was realized with a small deviation within the hypothesis Nr. 4.

We can conclude that the WAS solubilisation over 90% and recirculation of the LPH-WAS as a nutrient to the biological wastewater-treatment plant is an attractive solution if we consider it in terms of the reduction and re-use of solid waste. Especially when the latter is at the same time hygienised by the hydrolysis at pH 12 and 70 °C, so that it is suitable as raw material in the cardboard production, which gives the pulp-and-paper industry the possibility of implementing a “zero-sludge” concept. Such a re-integration of WAS back into the cardboard production and wastewater treatment can be considered as a sustainable method for the WAS treatment, which is worthy of upgrading to the large-scale level. On this basis, a patent application was made and the up-scaling within an eco-innovation-project started.

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