

Alkaline solubilisation of waste activated sludge (WAS) for soluble organic substrate – (SCOD) production

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Abstract: Improving the effects of hydrolysis on waste activated sludge (WAS) prior to anaerobic digestion is of primary importance. Several technologies have been developed and partially implemented in practice. In this paper, perhaps the simplest of these methods, alkaline solubilization, has been investigated and the results of hydrolysis are presented. An increase to only pH 8 can distinctively increase the soluble chemical oxygen demand (SCOD), and produce an anaerobic condition effect favorable to volatile fatty acids (VFA) production. Further increases of pH, up to pH 10, leads to further improvements in hydrolysis effects. It is suggested that an increase to pH 9 is sufficient and feasible for technical operations, given the use of moderate anti-corrosive construction material. This recommendation is also made having taken in consideration the option of using hydrodynamic disintegration after the initial WAS hydrolysis process. This paper presents the effects of following alkaline solubilization with hydrodynamic disintegration on SCOD.

Introduction

Excess or waste activated sludge is the main by-product from the biological treatment of wastewater. Although the amount of waste activated sludge (WAS) produced during treatment constitutes about only 1% of the total influent wastewater, the handling and disposal costs can be as high as 20 to 50% of capital and operational costs. This high cost is connected with the new regulations concerning WAS disposal. In the past, one relatively cheap option was to provide WAS for use on agriculture land. Although the use on agriculture land is still possible, the quality requirements, especially the microbiological constraints, impose complex treatment processes and necessitate strict monitoring. Also, because 100% safety in terms of pathogen removal cannot always be assured, there is some reluctance to use sewage sludge on agricultural land.

Regardless of the WAS treatment processes being applied, a minimization of the amount of sludge produced is of primary importance. To date, many alternative sludge handling processes (Rocher et al. 2001, Lin 2003, Ramakrishna and Virarghavan 2005, Zielewicz-Madej 2000) have been developed aiming at sludge reduction as well as pretreatment methods such as dewatering (Li et al. 2008, Neyens et al. 2003). Sludge disintegration has been extensively studied and

proved an improvement when used in combination with sludge reduction techniques.

Sludge disintegration methods include mechanical, chemical, thermal and biological treatments.

Mechanical processes are milling, homogenization or ultrasonic disintegration. Probably the most promising techniques are based on the phenomenon of hydrodynamic cavitation. Under the specific condition of water flowing through a constriction, like a valve, Venturi or Lavale nozzle, or even orifices (simple holes), a drastic pressure reduction occurs at the outflow. Dissolved air appears as micro-bubbles, which implode at high temperature and pressure (Clark 1997). The hydroxyl radicals are produced during the decomposition of complex organic substances at high local temperatures (Petrier and Francony 1997). The application of the hydrodynamic cavitation phenomenon to activated sludge disintegration – cell structure disruption – has been investigated by many authors (Kalumuck 2000, Gogate and Pandit 2005, Suschka et al. 2007a, 2007b, Grübel 2007).

Chemical disintegration processes are based on oxidation, by applying ozone (O₃) or hydrogen peroxide (H₂O₂), for example. Acidification or alkalization are also processes aiming at microbial cell solubilization. Alkaline disintegration is simple in terms of the necessary equipment and operation. It is also claimed to be highly efficient (Weemaes and Verstratete

1998). Alkaline sludge treatment can disrupt flocs and cells, release inner organic matter and accelerate hydrolysis. If applied as a sludge pretreatment before anaerobic digestion, the digestion process is expected to be more effective (Kim et al. 2003).

Alkaline sludge treatment can also release the water from inside flocs and cell structures, which cannot be removed by conventional dewatering processes. Therefore, alkaline treatment can improve sludge dewatering capability (Li et al. 2008, Neyens et al. 2003). The possibility of enhancing alkaline hydrolysis with gamma ray irradiation has been investigated by Kim et al. (2007). An increase of SCOD and VFA was demonstrated.

Some chemical disintegration processes – acidification or alkalization methods mainly – are often combined with thermal processes in a wide temperature range, from 70 to 200°C (Athanasoulia et al. 2007).

The aim of the investigations into sludge alkaline treatment has varied from improvement of sludge dewatering to enhancing the effectiveness of aerobic sewage treatment as well as WAS minimization. A small number of investigations have been dedicated directly to the effects of sludge hydrolysis as an anaerobic digestion pretreatment process for biogas production increase. Chen et al. (2007) investigated the effectiveness of anaerobic digestion at different pH values, from 4 to 11, concluding the best effects for methane production which can be achieved at a pH in the range 6 to 7.

The main aim of this study was to clarify, evaluate and elucidate the effects of sludge pre-hydrolysis procedures prior to anaerobic digestion. The study focused on the effects of using hydrodynamic WAS disintegration enhanced by pre-alkalization as a pretreatment process before sludge anaerobic digestion. The alkaline sludge treatment leads to the partial dissolution or destruction of flocs structure, and the swelling, and subsequent solubilization, of cell walls. It was expected that the combination of alkaline treatment and hydrodynamic cavitation would increase the soluble chemical oxygen demand (SCOD) and upgrade the effectiveness of anaerobic sludge digestion in terms of biogas production and sludge quantity minimization.

Materials and methods

Waste activated sludge (WAS) was sampled at a large municipal sewage treatment plant. The plant is operated according to the enhanced biological nutrients removal procedure, and uses no preliminary settling tanks. The total solids concentration in the sample taken from the thickening tank was about 13 g/dm³, and the organic matter content was around 67–72%.

For chemical WAS disintegration sodium hydroxide (NaOH) 2M was used. NaOH was added to samples of activated sludge in amounts sufficient to maintain a given pH value of 8–12 for 30 minutes. In addition to chemical hydrolysis as a result of alkalization – through the addition of NaOH – the use of hydrodynamic cavitation (disintegration) was also tested. Mechanical disintegration of a 25 dm³ of samples of activated sludge was executed in the process of hydrodynamic cavitation. The experimental set-up consisted of a 12 bar pressure pump, rating 0.54 kWh, output 500 dm³/h, which recirculated WAS from a container, through a constructed 1.2 mm nozzle. To force 25 dm³ of WAS through the nozzle

took 3 minutes. The process was carried out for 30 minutes, which corresponded to 10 multiplicity flow by cavitation nozzle. In our research, we decided to use a constructed cavitation nozzle with a diameter ratio of $\beta = d_0/d_1 = 0.30$ (d_0 – diameter narrowing; d_1 – diameter of inflow), which allows us to obtain a cavitation number of $\sigma = 0.245$, in selected flow conditions. Accordingly, the numerical results of the design of this device are relatively efficient – the calculated pressure loss is $p = 74.8$ kPa, whereas the net pressure drop ($p_{min}/\Delta p$) is almost five times greater.

The anaerobic digestion experiments were carried out in 1 dm³ reactors, with continuous mixing, placed in a thermostat at 35±1°C. Several series constituted a reference sample (reactor), and four reactors contained activated sludge corrected to a pH of 7, 8, 9 and 10, respectively, by the addition of NaOH. The process of anaerobic digestion was continued for 6 days.

All chemical analyses were performed for samples before and after each phase of disintegration and during anaerobic digestion. Daily samples were taken to determine the soluble chemical oxygen demand (SCOD), pH, oxidation reduction potential (ORP) and volatile fatty acids (VFA). Determinations of total and organic solids were performed at the start and end of the experiments. Total solids (TS), volatile solids (VS), soluble chemical oxygen demand (SCOD) were determined following the standard methods for examination of water and wastewater procedures 2540G and 5220D, respectively (Rice et al. 2012). VS were measured in triplicate. To analyze the soluble phase, the particulate sludge matter was removed by centrifugation (10 min at 5000 rpm), and the resulting centrate was filtrated through 0.45 µm pore size membrane filters. For colorimetric determinations, a spectrophotometer XION 500 Dr Lange was applied. The pH and conductivity measurements were carried out with a WTW inoLab Level2 meter, equipped with a SenTix K1 electrode for pH.

Results and discussion

According to the methodology applied during the experiments, the amount of alkaline (NaOH) addition was such as to get the desired pH after 30 minutes. This initial period was set to allow chemical reactions and the penetration of activated sludge flocs. Subsequent determinations showed a rapid decrease of pH. Simultaneously, an increase of soluble chemical oxygen demand (SCOD), reaching an almost constant level was achieved (Fig.1). The time to achieve the constant level of SCOD concentration depended on the desired alkalization, i.e. the intended pH. The constant level could be interpreted as the maximum degree of chemical hydrolysis which possible to achieve for a given pH.

The SCOD values achieved after chemical hydrolysis and after 3 days in anaerobic conditions are shown in Fig. 1. It can be seen that the values of SCOD are much higher for an initial pH 10 in comparison to those achieved with lower initial values of pH.

The intensity of this process depends on the initial pH. For initial pH of 7, 8, 9 and 10, the respective solubilization times were approximately 55, 50, 30 and 15 hours (Fig. 2).

As already mentioned, the aim of activated sludge chemical hydrolysis is to increase sludge decomposition and, in time, minimize the amount of WAS to be disposed. Released

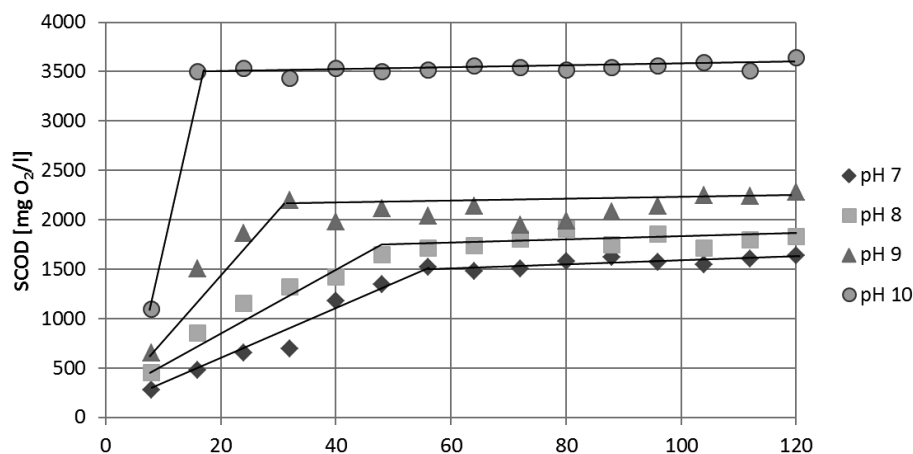


Fig. 1. Solubilization effects of alkalization with time

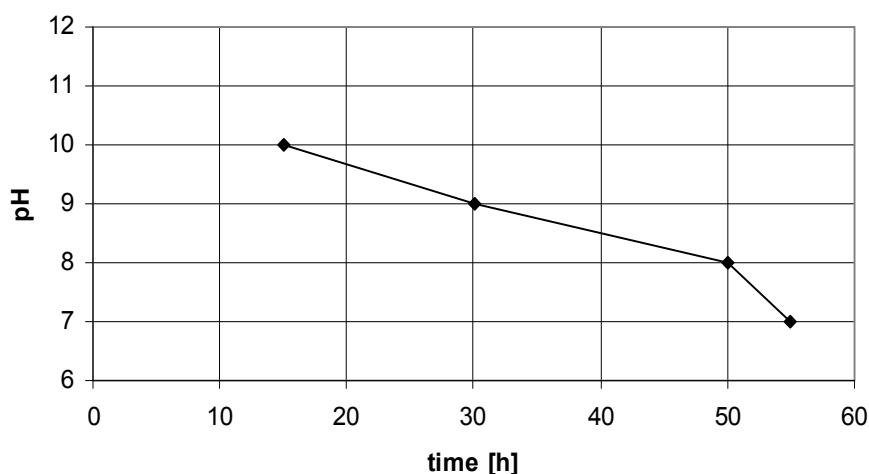


Fig. 2. Time elapsed before reaching a quasi-constant solubilization effect

organic matter expressed as SCOD should allow for faster degradation in the anaerobic digestion process, thus reducing the retention time and resulting in a higher biogas production.

Simplifying the anaerobic sludge digestion process, and distinguishing only two stages, the first stage of hydrolysis and the second stage of acidification, is regarded as the rate limiting step.

The most interesting question, in the context of these investigations, is to what extent the degree of alkalization can disturb (e.g. biomass decomposition rate) or enhance the anaerobic digestion acidification stage. Waste activated sludge with a pH in the range of 6.64–6.88 was tested. When the pH was increased to 8, 9 and 10, after 30 minutes of NaOH addition, no negative effects were observed. For samples with initial pH values of 8 and 9, after 1.5 days the pH stabilized between 7.3 to 7.4. Only samples with an initial pH of 10 required a much longer time to reach a level of pH 8.

It has to be stressed again that the process of alkalization is a pre-hydrolysis process. It means that the initial pH of the WAS discharged to the anaerobic digester with, say, a 20 days detention time – i.e. the WAS comprises 1 in 20 of the digester's volume – has a very limited effect on the pH of the content in the digester. Leaving the alkalized sludge

under anaerobic digestion for several days, leads to a distinct pH decrease as a result of biological processes. Remaining the alkalized sludge under anaerobic digestion for several days, there is a distinct pH decrease as a result of biological processes as shown in Fig. 3.

For samples with an initial pH 7 the maximum concentration of VFA (660 mg/l) was measured after 80 hours. After the same period, the respective values for samples with initial pH 8 and pH 9 were 770 and 1000 mg/l (Fig. 4).

For samples with an initial pH 10 no maximum concentration of VFA was reached. For a digestion time of 80 hours, 1680 mg/l of VFA was produced. The different concentrations of VFA produced for the various initial values of pH are clearly shown in Fig. 4.

As shown above (Fig. 4), undertaking chemical hydrolysis of WAS before anaerobic digestion allows for a drastic increase in the production of volatile fatty acids.

Organic matter solubilization can be further enhanced if hydrodynamic disintegration is incorporated into the process. Hydrodynamic disintegration, evoking the phenomenon of cavitation, is a very effective activated sludge destruction process. However, this process is associated with a relatively high power consumption. Hydrodynamic disintegration

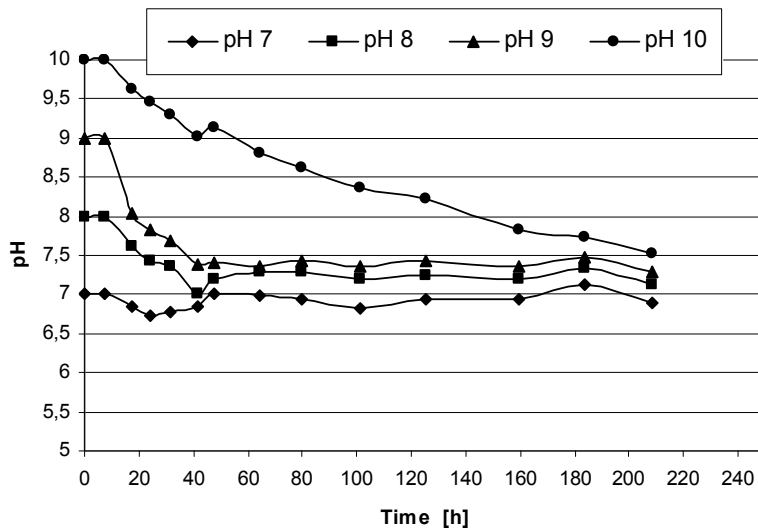


Fig. 3. Decrease of sludge initial pH with time of anaerobic conditions

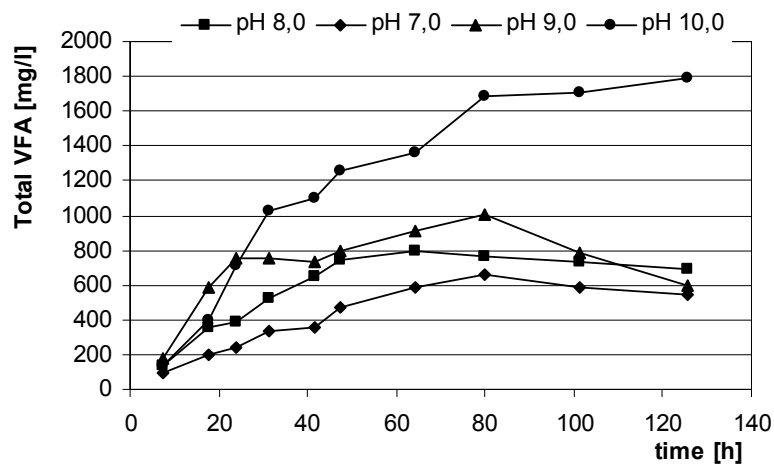


Fig. 4. Volatile fatty acids (VFA) produced in the course of anaerobic digestion

executed for 30 minutes (Suschka et al., 2007a and 2007b) can achieve an increase of SCOD in the liquid associated with the activated sludge by a factor of approximately 2.5. Somewhat better results can be obtained by hydrolysis, through the process of alkalization to pH 9. A combination of the two processes – disintegration and alkalization (to pH 9) – results in further increase of activated sludge hydrolysis. The results are shown in Fig 5.

Fig. 5 shows the results for WAS hydrodynamic disintegration, for chemical hydrolysis and for a combination of a pH increase to pH 9 and consecutive hydrodynamic disintegration. The four different samples of WAS used to compile the results for each procedure presented in Fig. 5 were collected at different periods, and the results are organized from the lowest to the highest values of SCOD obtained under each procedure. The samples were randomly selected for WAS with biomass concentration of around 9 500 mg/dm³.

The definitively higher results obtained for the procedure involving the hydrolysis of WAS samples (spiked with NaOH to increase the pH to 9) and consecutive hydrodynamic disintegration are the result of preliminary

softening of the bacteria cell walls and dissolution of external polymers. Investigated pretreatment technology resulted in an increase of biogas production (Grübel and Machnicka 2009, Grübel et al. 2013). Optimization of the required hydrodynamic disintegration process as well as the selection of the optimum alkalization rate seems to be the way to enhance the process of anaerobic waste activated sludge digestion. It has to be stressed once again that an initial pH of 9 does not have a negative effect on VFA production, but on the contrary, a positive effect.

Conclusions

1. Alkalization of waste activated sludge (WAS) is a sludge hydrolysis process that requires a compromise between the amount of alkaline addition, using, for example, sodium hydroxide (NaOH) and time of reaction.
2. Here, the initial reaction time was randomly selected as 30 minutes. The measured pH at the end of that period was accepted as the level of alkalization.
3. The detention of alkalized WAS in anaerobic condition results in a relatively slow pH decrease. After approximately 2 days

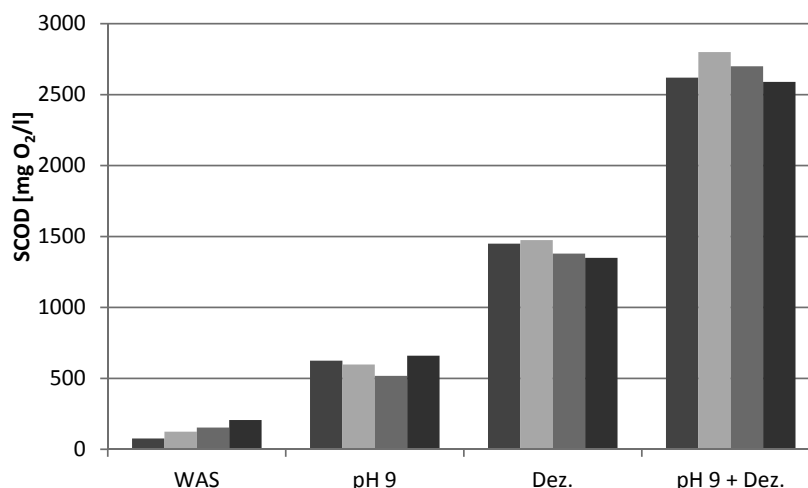


Fig. 5. Solubilization effects of investigated procedures – results from four different WAS samples
 WAS – SCOD in waste activated sludge liquor; pH 9 – alkaline solubilization of WAS; Dez. – hydrodynamic disintegration for 30 minutes; pH 9 + Dez. – alkaline hydrolysis and post hydrodynamic disintegration

the pH decreases to a semi-constant level, of between 7.0 and 7.4 for samples with an initial pH of 8.0 or 9.0. However, for samples with an initial pH of 10.0, a much longer time of approximately 10 days is required to lower pH to about 7.5.

4. It was concluded that alkalization to a pH of 9.0, which results in an average increase of SCOD by a factor of 3.2, is satisfactory and it is safe in terms of consecutive biological anaerobic digestion processes, including the

first stage of acidogenesis – the production of volatile fatty acids (VFA).

5. A very promising procedure of enhancing WAS hydrolysis is alkaline addition followed by hydrodynamic disintegration. Chemical hydrolysis, as a result of pH increase (say to pH 9), weaken the bacterial cells and dissolve external polymers, thus distinctively improving the effects achieved by mechanical disintegration.

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Tworzenie się rozpuszczalnego substratu organicznego podczas zasadowego rozpuszczania osadów ściekowych

Zastosowanie wstępnej hydrolizy osadu czynnego wpływa w znaczący sposób na poprawę efektów fermentacji beztlenowej. W pracy przedstawiono wyniki wstępnej alkalizacji osadu. Stwierdzono, że w wyniku wzrostu pH do 8 nastąpiło wyraźne zwiększenie ChZT w cieczy nadosadowej i intensyfikacja produkcji LKT, a zmiana odczynu do pH 10 powoduje zwiększenie efektów hydrolizy. Wykazano, że wstępna hydroliza osadu do pH 9 jest możliwa do zastosowania w praktyce, z uwagi na wykorzystanie materiałów konstrukcyjnych o umiarkowanej odporności na korozję. Po wstępnej alkalizacji możliwe jest stosowanie innych metod dezintegracji osadu. W pracy przedstawiono wyniki kondycjonowania osadu poprzez alkalizację w połączeniu z dezintegracją hydrodynamiczną.