



EFFECT OF MICROWAVE ASSISTED ALKALI AND ACIDIC PRE-TREATMENT ON THE BIODEGRADABILITY OF DAIRY SLUDGE

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Abstract

Advantageous effects of microwave pre-treatment on biodegradability of different kind of wastewater sludge have been verified in many papers. Chemical pre-treatments are also suitable to increase the disintegration degree and to enhance the biogas production from sludge. Combination of microwave irradiation with chemical methods could be a promising pre-treatment process for enhanced biodegradability. Combined microwave-alkaline pre-treatment methods are more commonly used for sludge pre-treatments than microwave-acidic method. Therefore, our aim was to investigate the effect of microwave assisted alkali and acidic pre-treatment on organic matter release from sludge and biodegradability. Our results verified that beside microwave-alkaline pre-treatment methods, the microwave-acidic process is suitable as potential pre-treatment method, but particularly is capable for enhanced aerobic biodegradability of dairy sludge.

Keywords

microwave, sludge, biodegradability, pre-treatments

1. Introduction

Attention to microwave heating applications is continuously growing, because of the special mechanisms of microwave irradiation for energy transfer. On the contrary of the conventional heating mechanisms, energy is delivered directly into the materials during microwave heating due to the molecular level interactions with high frequency electromagnetic field. Because of the high energy density and volumetric heating effect, microwave irradiation is suitable to achieve very short process time, and, in some cases, microwave irradiation induces special structural properties or new way for chemical reactions (Kappe, 2004).

Depending on the physicochemical structure and composition of processed material, and the applied frequency range, heating mechanisms of microwave irradiation is occurred by dielectric polarization and/or ionic conduction. Orientation polarization or dipole rotation occurs due to the reorientation of permanent dipoles in oscillating electromagnetic field (Barba and D'Amore, 2012). The materials containing free electrons charge polarization can be observed caused by the modification of position of electrons, resulted in non-uniform distribution of charges.

In the industrially scale used microwave frequency ranges, and mainly for high water contented materials the dipole rotation is

the dominant mechanisms, but ionic dissipation phenomena can be also occurred, if ions are presented in the irradiated materials (Brodie et al., 2014). In complex structured materials both mechanisms can be determinative at the same frequency, for example if the state of water content is changed. If thermal or mechanical stress was applied cell walls can disrupt, therefore the intracellular components are released increasing the free water content.

Extracellular polymer substances (EPS) of sludge form a complex physicochemical structure with low bioavailability. In raw sludge the organic matters are presented in particulate form, what decrease the theoretically achievable biodegradation rate (Neyens et al., 2003). In primary sludge, especially if it is produced from food industry effluents, macromolecular components are the main part of organic matter content. Divalent cations bind to polysaccharides and proteins of EPS matrix form connected structures of micro-flocs, and increase the size and stability of sludge floc. Therefore, in most cases pre-treatments are need to increase the availability of substrate before biological utilization of sludge.

Among the thermal pre-treatment methods microwave irradiation could be a promising alternative for process operated by conventional heating. Microwave has strong effect on microbial destruction, microwave process need significantly shorter time demand than needed for conventional heat treatments. Depending on the heating rate and final temperature during the processes, with the application of microwave pre-treatments higher disintegration degree can be achieved. Therefore the higher disintegration degree and higher organic matter solubility led to higher biogas yield in AD process.

Beside absolute value of biogas production, the biogas production rate presents key issue to evaluate the efficiency of a pre-treatment method. Efficiency of microwave pre-treatments depends on the type and condition of anaerobic digestion. Thermophilic digestion suitable to achieve higher biogas product, the effect of pre-treatments are slightly than that of obtained for mesophilic temperature ranged AD tests (Koupaie and Eskicioglu, 2016).

Alkaline treatments, especially if it is associated by thermal methods, suitable to increase the disintegration, accelerate the anaerobic digestion and enhance the biogas production, as well (Dogan and Sanin, 2009). For alkaline pre-treatments NaOH is more effective than $\text{Ca}(\text{OH})_2$ (Kim et al., 2003). But overdosing of NaOH can decrease the efficiency of bicarbonate buffer system

of anaerobic digesters, inhibiting the decomposing activity of anaerobic microorganisms. Appropriate alkaline dosage is efficient for floc disintegration but strong alkali condition should be avoided if sludge contains lipids, because of the saponification reactions.

Researches verified that ultrasonic-acid pre-treatment of municipal waste activated sludge (WAS) the release of organic matter and disintegration degree can be improved, if pH decreased. Shear forces generated by sonication disrupt the flocs then macromolecular components are more effectively exposed to H⁺ ions (Sahinkaya, 2015). Pre-treatment of municipal WAS under acidic condition led to 4-6 times increment of carbohydrate and protein solubility. In batch mesophilic AD tests biogas production increased by 17% and 32% if acidic treatments were carried out at pH 2 and pH 1, respectively.

2. Materials and Methods

Sludge sample was originated from the sedimentation tank of the primary wastewater treatment line of a dairy factory. Sludge samples were kept refrigerated before processing. Dairy sludge has TS and COD content of 3.2% and 21100 ± 320 mgL⁻¹, respectively

Microwave pre-treatments were carried out in a tailor made continuously flow operated microwave equipment. The magnetron operated at a frequency of 2450 MHz, power was changed continuously in the range of 100 to 700W. Sludge flow through the microwave reactor was ensured by peristaltic pump.

Specific microwave irradiated energy (E_s , kJ L⁻¹) was determined from the volumetric flow rate (Q , Ls⁻¹) and the power of magnetron (P_m , W).

$$E_s = \frac{P_m}{Q} \text{ (kJ L}^{-1}\text{)} \quad (1)$$

Alkali and acidic treatments were carried out before entering the sludge into the microwave reactor dosing NaOH or H₂SO₄, respectively.

Anaerobic biodegradability was characterized by biogas production determined by batch mesophilic anaerobic digestion (AD) tests. Biogas production was measured at 37 ± 0.5°C for 30 days by pressure increment method. AD tests were carried out continuously stirred sealed serum bottles bottle with volume of 250 mL. The change in headspace pressure was detected by OxiTop® Control (WTW, Germany) manometric measuring heads in an interval of 12 hrs..

Biogas volume was calculated from the pressure increase and the volume of headspace using the ideal gas law. pH of sludge samples was adjusted to 7.2 before the AD tests. Biogas yield was given for total solid (TS). For seeding municipal digested sludge was used from an operating anaerobic digester.

Biodegradability under aerobic condition was characterized by the change of biochemical oxygen demand (BOD) in the soluble fraction of organic matters. Biochemical oxygen demand was measured in a respirometric BOD system thermostated at temperature of 20°C for 5 days.

3. Results and Discussion

Results of AD tests show, that both the alkaline and acidic pre-treatment assisted by microwave irradiation verified suitable to increase the biogas yield from dairy sludge. Exposed the sludge to MW irradiation with E_s of 220 kJ L⁻¹ and MW power of 536W carried out alone (without chemical dosage) biogas yield of near 400 mL gTS⁻¹ could be achieved (Figure 1.). Biogas production for combined MW/chemical pre-treated sludge was influenced by the E_s and microwave power, as well.

At lower power level (536W) and using lower alkaline dosage (0.2 and 0.35 gNaOH/gTS) increasing of NaOH dosage or irradiated MW energy led to increased biogas yield (Figure 1.a). At higher power level (700W) there was not observed further significant increment in biogas production when energy intensity was increased from 170 to 220 kJ L⁻¹ or the concentration of added NaOH was increased from 0.35 to 0.5 gNaOH/gTS (Figure 1.b).

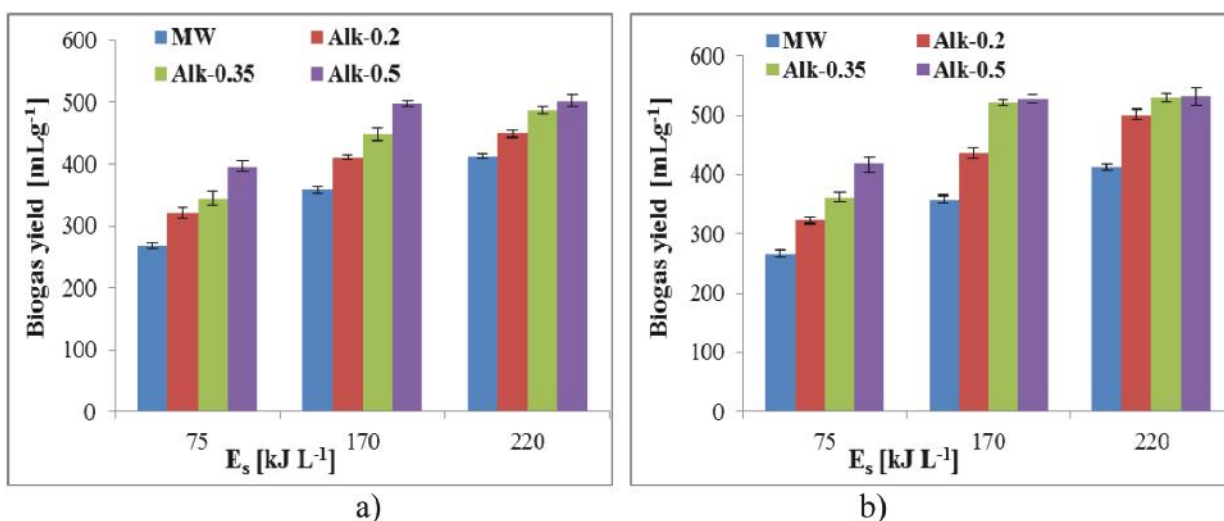


Figure 1. Biogas production of microwave-alkaline pre-treated sludge (MW power of 536W (a) and 700W (b))

Considering the effects of microwave/alkaline pre-treatment can be concluded that for achieving the same biogas yield enhanced energy intensity enable to reduce the alkaline dosage, or rather, increased alkaline dosage make possible to decrease the energy intensity of MW irradiation. From energetically aspects,

alkalization of sludge improve the biogas production, and alkaline dosage before thermal pre-treatment of sludge make suitable to reduce the energy demand of microwave process.

Compare the effect of combined acidic/microwave pre-treatment on biogas yield to that of obtained from

alkaline/microwave process it can be summarized, that acid dosage improve the biogas yield, but achievable maximum biogas

yield is lower than that of determined for alkaline pre-treated samples (Figure 2.).

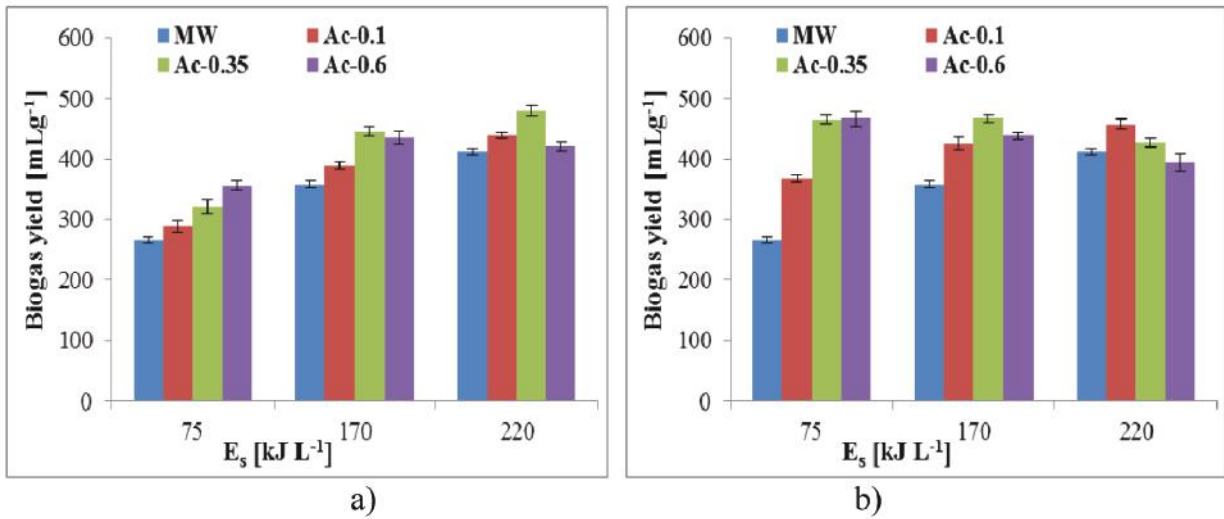


Figure 2. Biogas production of microwave-acid pre-treated sludge (MW power of 536W (a) and 700W (b))

In the case of microwave irradiated sludge dosed acidic before pre-treatment, the enhancement of energy intensity with increased acid dosage can led to decreasing tendency of biogas production. At 536W power level and applying energy intensity of 220 kJ L⁻¹ enhanced acid dosage from 0.35 to 0.6 g H₂SO₄/gTS cause 11% decreasing in biogas yield (Figure 2.a). At higher power level (700W) the same tendency (peak value followed by decreasing in biogas yield) was observed for pre-treatment with 170 and 220 kJ L⁻¹ (Figure 2.b). Increasing of microwave power under acidic condition contributed to take place chemical reaction between the organic components derived from partially hydrolyzed macromolecules which

produce heavily biodegradable and less soluble product (Takashima and Tanaka, 2014).

For comparison purposes, the shorter time biodegradation of microwave irradiated and acidified or alkalinized sludge samples was also examined under aerobic condition. For characterization of aerobic biodegradability the biochemical oxygen demand was measured for 5 days from the separated soluble organic matter fraction of sludge. Similarly to the results obtained for anaerobic digestion it was found that microwave irradiation applied alone is suitable to increase the concentration of biodegradable organic matters, as well (Figure 3.). Increment of BOD was influenced by the energy intensity and the chemical dosage, as well.

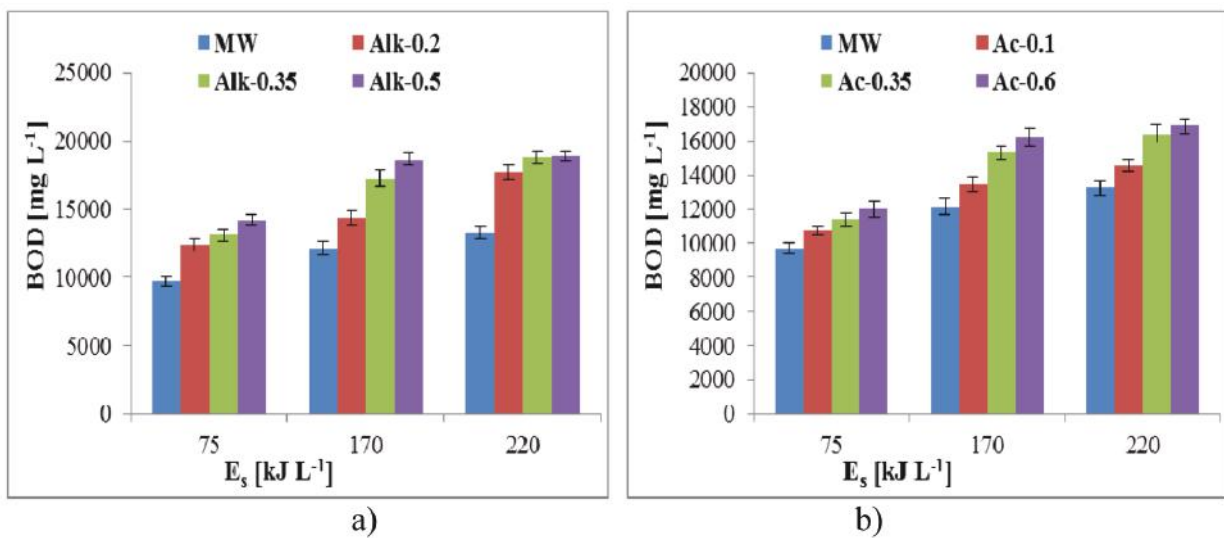


Figure 3. BOD of alkaline (a) and acidic (b) MW pre-treated sludge (MW power=536W)

Applying of acid/alkali dosage followed by microwave irradiation increased further the biodegradability of sludge. Alkaline pre-treatment enhance the efficiency of sludge flock disintegration during thermal processes, therefore improve the substrate availability for decomposing microorganisms (Dogan

and Sanin, 2009). Acidic condition assists in the disruption of extracellular polymeric substances and hinders the reflocculation (Liu et al., 2016). These establishments related to municipal waste activated sludge were verified for dairy sludge, as well.

Acid dosage and as well as alkaline dosage combined the intensive heating effect of microwave irradiation were suitable to increase the BOD. Maximum achievable BOD concentration was higher for alkaline method than for acidic/microwave pre-treatments. Using the same range of Es, microwave power and alkaline/acidic dosage than was applied before AD tests decreasing tendency of BOD was not observed if Es or acid dosage increased.

4. Conclusion

In our work the applicability and efficiency of microwave irradiation combined with acid/alkaline dosage, as thermochemical pre-treatment method, was investigated. Our results show, that microwave irradiation alone was suitable to increase both the aerobic and the anaerobic biodegradability. Pre-treatments, where sludge alkalization was combined with microwave irradiation the biogas production enhanced, but the effect of two methods could not be considered synergetic. Increased microwave power or irradiated energy enables to reduce the alkaline dosage to achieve the same biogas yield. Microwave treatment under acidic condition increased the aerobic biodegradability, but beyond a certain value of irradiated energy level or acid dosage decreasing tendency was found in the change of anaerobic digestibility. Our results verified that beside microwave-alkaline pre-treatment methods, the microwave-acidic process is suitable as potential pre-treatment method, but particularly is capable for enhanced aerobic biodegradability of dairy sludge

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