

Electrochemical and biological treatment of return liquors from dewatering thermal hydrolysis digestate

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Abstract: Organic, mostly refractory compounds and ammonium in return liquors from dewatering thermal hydrolysis (TH) digestate were degraded to a large extent using a boron-doped diamond electrode. Electrochemical pre-treatment slightly improved biodegradability of organics but inhibited nitrification. The electro oxidation of biologically pre-treated return liquor at a lower current density was significantly more effective regarding COD degradation and energy demand.

Keywords: Thermal hydrolysis; return liquor treatment; electro oxidation

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Introduction

Thermal hydrolysis of waste activated sludge has experienced increasing interest in recent years as the growing number of commercial full scale plants reflects. The significant improvement of anaerobic biodegradability and improved dewaterability face higher ammonium concentrations and the formation of refractory compounds (Barber, 2020). Elevated temperatures, typically between 130 to 170 °C, lead to simultaneously increasing share of biological refractory compounds. Refractory soluble chemical oxygen demand (COD) in return liquors from dewatering thermal hydrolysis digestate was found to be about 60 - 70 % and can significantly affect effluent COD concentration (Toutian et al., 2020). Further treatment processes are necessary to remove refractory COD, including e.g. electrochemical advanced oxidation processes with boron-doped diamond electrodes. Besides direct electron-transfer and oxidation by hydroxyl radicals formed on the surface of the anode, bulk oxidation of COD and ammonium is possible due to the formation of chlorine to hydrogen peroxide (Liakos et al., 2017).

Material and Methods

The return liquor from dewatered thermal hydrolysis digestate derived from a municipal wastewater treatment plant in Germany. The TH unit was operated at approx. 157 °C in the bypass of a mesophilic digester. All samples were filtrated (0,45 µm Nylonmembran, Merck, Germany) and analysed as duplicates in terms of COD, dissolved organic carbon (DOC), ammonium, nitrate, nitrite, chloride (Table 1.1).

Table 1.1 Characterization of TH return liquor and methods used

<i>Parameter</i>	<i>Value</i>	<i>Method</i>
COD [mg/l]	854 ± 33	LCK514/ LCK314
DOC [mg/l]	266 ± 16	DIN EN 1484
NH ₄ -N [mg/l]	906 ± 32	LCK303
NO ₂ -N [mg/l]	<1	DIN EN ISO 10304-1
NO ₃ -N [mg/l]	<1	DIN EN ISO 10304-1
Cl ⁻ [mg/l]	1,548 ± 49	DIN EN ISO 10304-1

Figure 1.1 gives an overview of the experiments.

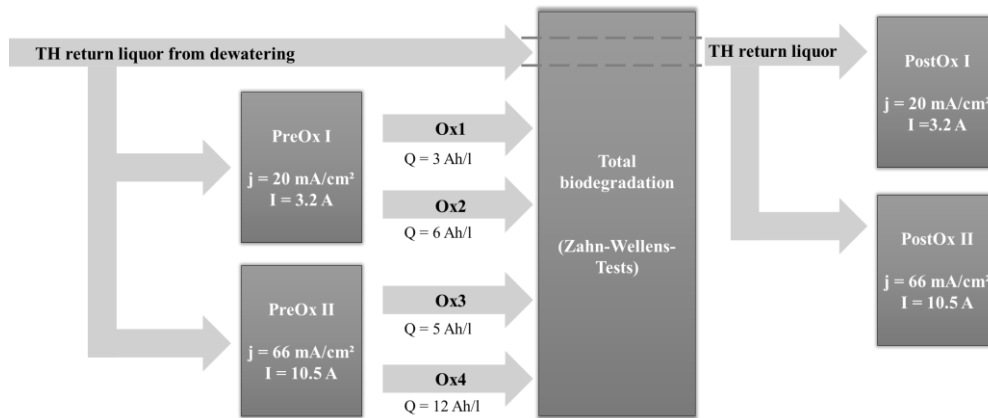


Figure 1.1 Graphical abstract

For the electrochemical oxidation, a boron-doped diamond electrode (Type “Susi”, DiaCCon, Germany) with an anode surface of $A = 0.016 \text{ m}^2$ was used and fed via a recirculation tank ($V = 15 \text{ l}$) at constant temperature. Prior to oxidation, return liquor was filtrated coarsely to avoid blocking of the electrode. Samples taken during experiments were stored at $8 \text{ }^\circ\text{C}$ and filtrated the next day. Biodegradability was measured in triplicates using Zahn-Wellens-Tests according to DIN EN ISO 9888, but incubated for 42 days. Temperature was $23^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$, oxygen was ensured to be $>4 \text{ mg/l}$ and pH was adjusted regularly.

Results and Conclusions

Removal of COD was higher for 20 mA/cm^2 than for 66 mA/cm^2 , but both were significantly lower than the maximum COD degradation (Figure 1.2, a). This can be attributed to side reactions, which consume current and reduce efficacy. The anodic degradation of COD was under mass transfer control ($j_{\text{app}} > j_{\text{lim}}$) and modelled according to equation (1) (Liakos et al., 2017). Mass transfer coefficients k_m were conducted from experimental results and were 7.0×10^{-6} and $1.5 \times 10^{-5} \text{ m/s}$ for 20 mA/cm^2 and 66 mA/cm^2 . Smaller k_m and higher COD degradation for 20 mA/cm^2 indicate that oxidation processes in the bulk phase became increasingly relevant for COD degradation. Additionally, bulk oxidation processes like the oxidation of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$, N_2 by hypochlorous acid were present (Figure 1.2, b).

$$COD(t) = COD_0 \cdot \exp\left(-\frac{A \cdot k_m \cdot t}{V}\right) \quad \text{Eq. (1)}$$

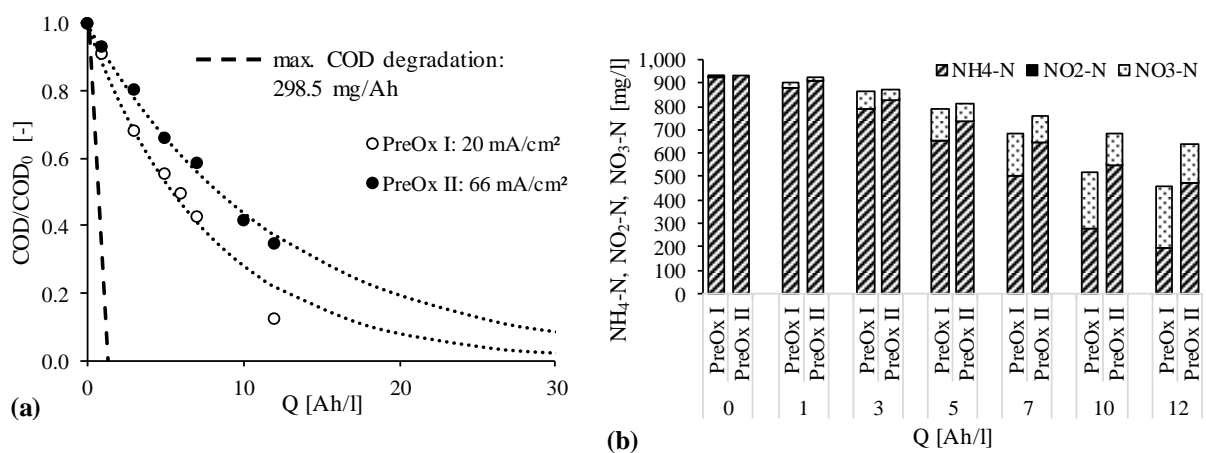


Figure 1.2 Evolution of COD (a) and ammonium (b) during the oxidation of return liquor

Biological degradation of TH return liquor was 17.2 % after 42 days of incubation, which in turn corresponds to a refractory organic matter content of 83.8 % (Figure 1.3, a). The electrochemical pre-treatment led to an increase of DOC concentration in the first couple of days. This was possibly caused by the degradation of biomass resulting from electrochemical pretreatment by-products. Further on, biological degradation was slightly higher for 66 mA/cm² as DOC was removed by 19.4 % (Ox 1) to 26.6 % (Ox 4). Overall, 66 mA/cm² showed no positive effect, since electrochemical removal was lower. Associated with this, NH₄-N removal by nitrification was only about 19 - 30 %, while almost 100 % were reached in TH return liquor. Degradation of biomass may be due to Cl⁻, which oxidized to ClO₃⁻ and ClO₄ during electro-oxidation (Figure 1.3, b).

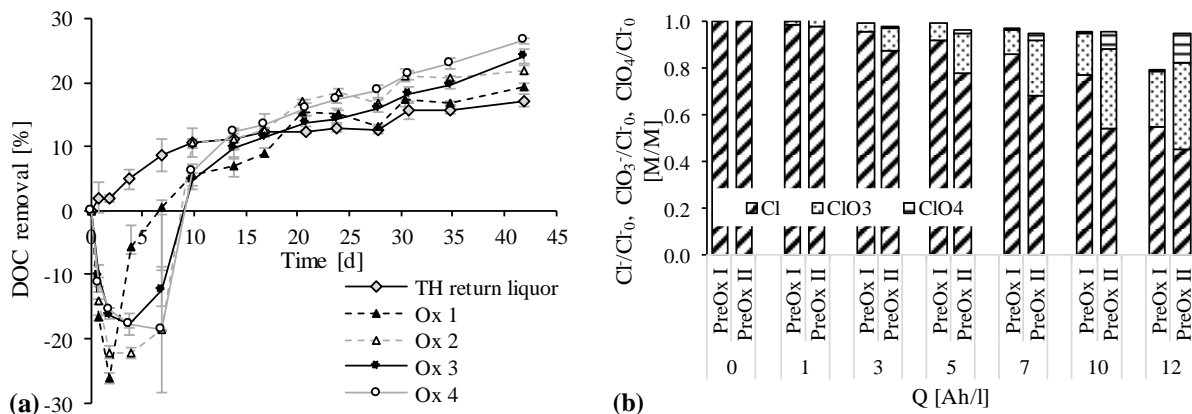


Figure 1.3 Removal of DOC during Zahn-Wellens-Tests (a) and evolution of chloride (b)

COD degradation of the biologically pre-treated return liquor was more quickly than for the untreated TH return liquor (Figure 1.4, a). Mass transfer coefficients were 2.5×10^{-5} m/s and 5.1×10^{-5} m/s for 20 mA/cm² and 66 mA/cm². Oxidation of COD in the bulk phase could be of greater significance, as NH₄-N was already removed during biological degradation. This results in a considerably lower COD-specific energy demand for the biologically pre-treated wastewater (Figure 1.4, b). The current density of 20 mA/cm² was more energy efficient due to higher COD degradation on the one hand and a lower voltage on the other hand. Overall, lower current density was advantageous for the degradation of pollutants, but also extended treatment time more than three times.

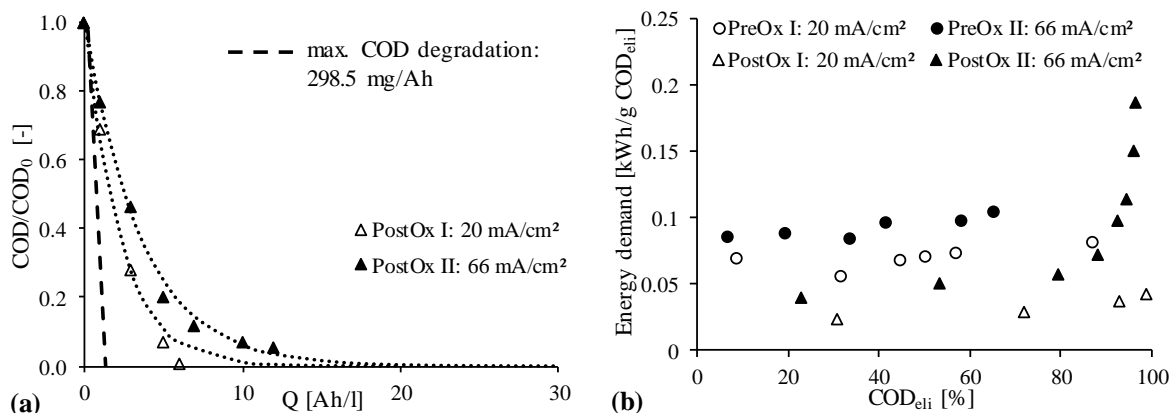


Figure 1.4 Evolution of COD during oxidation of pre-treated return liquor (a) and energy demand (b)

References

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