# Volume Optimization of Aerobic Digester for the Biodegradation of Plant Tannins in Industrial Wastewater

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Incorporating sustainability issues into pulp, paper and wood industry requires attentive design and operation of industrial wastewater treatment plants. Therefore, the main objective of this paper is volume optimization of two in-series connected aerobic digesters for the biodegradation of plant tannins in industrial wastewater. For this purpose some experiments were performed in laboratory bench top aerobic digester provided data used for kinetic parameters' determination. Afterwards, we estimated the total optimal volume of two-stage aerobic digester using criterion of a minimal total holding time. The excellent performance of applied criterion was proven with a more than two times lower total digester volume compared to one-stage plant.

#### 1. Introduction

Tannins are defined as water-soluble polyphenolic compounds of varying molecular weight (Makkar, 2003). They have traditionally been used for converting animal hides into leather, due to their ability to interact and precipitate proteins found in animal skin (Bisanda et al., 2003). Basic tannin production for tanneries is progressively being transmitted into a wide range of industrial applications – especially those aimed at the preservation and support of a healthier environment. Tannins are known to be toxic to many microorganisms (Field and Lettinga, 1992). Furthermore, their inhibition properties have a large impact on the antioxidant activities of many products (Alamprese et al, 2005; Mihara et al., 2005). On the other hand, tannins are also natural organic pollutants (Svitelska, 2004). They are present in pulp, paper and wood processing wastewaters (Vidal and Diez, 2005; Field et al., 1988). New requirements in the world global market with regard to sustainable development provides for more attentive wastewater management. Therefore, the major concern is to treat wastewaters before they are released into the environment.

There are many methods available for the removal of tannins from industrial wastewater (Svitelska et al., 2004; Bhat et al., 1998; Arana et al., 2001; Field and Lettinga, 1991). The activated sludge process (ASP) is the most generally applied biological wastewater treatment method (Gernaey et al., 2004). It is performed by a variable and mixed community of micro-organisms (biomass) in an aerobically aquatic environment. The biomass derives its energy from carbonaceous organic matter (COM) in wastewater which produces new cells, whilst simultaneously releasing energy through the degradation of this organic matter. The overall indicator of COM in wastewater is chemical oxygen demand (COD) (Gray, 2004). The main component of the ASP is a continuous-flow aerated biological reactor (aerobic digester) (Bailey and Olis, 1986).

Over recent years wastewater management has become a significant cost factor and an important aspect of the sustainable development. Consequently, the optimal design and operation of an aerobic digester are very important. Although wastewater treatment plants are linked by large investments, the aerobic digesters they contain are usually designed using extremely simplified and idealized kinetic models. Owing to insufficient literature available in this field, our previous work (Tramšek et al., 2006) determined the degradation rate of plant tannins in industrial wastewater based on a biochemical experimental method using tannins' mass concentration measurements. The COD method (ISO 6060: 1989(E), 1989) is an alternative method of following tannins' degradation rate indirectly.

The main intention of this study was to design an aerobic digester for the degradation of those plant tannins presented in industrial wastewater. For this purpose the parameters of the supposed inhibition kinetic model (using COD experimental measurements) were determined first. The tannins' biodegradation rate versus concentration curve shows a similar shape (with characteristic maxima) as that one for autocatalytic reactions. It is well known that, for the optimal reactor design in this case, the criterion of a minimal total holding time (MTHT) of a two in series connected CSTR should be applied. Therefore, optimal volumes regarding industrial wastewater capacity and wastewater treatment efficiency were established in the second part of the research.

#### 2. Materials and methods

#### 2.1 Industrial wastewater

Industrial wastewater (liquid waste stream after the extraction of tannins from chestnut chips) used in the laboratory research was obtained from the existing industrial production plant. In addition to dissolved plant tannins, wastewater also contains other dissolved organic compounds. The COM (tannins and other organic compounds) mass concentration in industrial wastewater indicated as COD was,  $\gamma_{\text{COD,I}} = (5.10 \pm 0.10) \text{ kg/m}^3$ . The tannins' chemical analysis using the UV spectrophotometric method (ISO 9648: 1988-12-15, 1989) showed that their mass fraction regarding overall COM was,  $w_{\text{T,i}} = (31 \pm 2)$  %.

#### 2.2 Kinetic model development

The process scheme (Fig.1) of two unequal (different volumes) in-series connected aerobic digesters can be described by a cascade of two CSTR (Levenspiel, 1999).

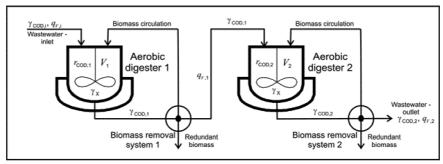


Figure 1: Process scheme of two unequal in series connected aerobic digesters.

If we assume equal inlet and outlet industrial wastewater volume flow rates ( $q_{V,i} = q_{V,1} = q_{V,2} = q_V$ ) then the degradation rate of COM expressed as COD,  $-r_{COD}$ , using the CSTR model under steady state conditions, can be described separately for aerobic digester 1 and 2, by equations as follows:

$$-r_{\text{COD,1}} = (1/Y_{\text{X/COD}})\mu\gamma_{\text{X}} = (q_{\text{V}}/V_{\text{I}})(\gamma_{\text{COD,i}} - \gamma_{\text{COD,1}})$$

$$\tag{1}$$

$$-r_{\text{COD,2}} = (1/Y_{\text{X/COD}}) \mu \gamma_{\text{X}} = (q_{V}/V_{2}) (\gamma_{\text{COD,1}} - \gamma_{\text{COD,2}})$$
 (2)

where:  $\gamma_{\rm COD}$  – mass concentration of COM (expressed as COD), V – volume of aerobic digester,  $\gamma_{\rm X}$  – mass concentration of biomass and  $Y_{\rm X/COD}$  – yield (biomass regarding COM). Traditionally, for wastewater treatment plants design and optimization purposes, the specific growth rate,  $\mu$ , is described using simplified and idealized Monod kinetics (Bailey and Olis, 1986). However, the Monod equation is unsuitable in the presence of toxic compounds, which inhibited biomass growth. Therefore, some other general formulas considering inhibition were found in the literature (Burhan et al., 2005; Loperena et al., 2006; Gokulakrishnan and Gummadi, 2006). It is well-known that inhibition appears during the biodegradation of phenolic wastewater (Hsien and Lin, 2005). Consequently, we assumed that biomass growth during COM degradation in industrial wastewater was based on Aiba's inhibition kinetic model (Aiba et al., 1968):

$$\mu = \left(\mu_{\text{max}}\gamma_{\text{COD}}/(K_s + \gamma_{\text{COD}})\right) \exp(-\gamma_{\text{COD}}/K_{\text{IA}})$$
(3)

where:  $\mu_{\text{max}}$  – maximum specific growth rate of biomass,  $K_s$  – saturation constant for COM, and  $K_{\text{IA}}$  – Aiba's inhibition coefficient. Different assumptions, well-known from literature, were applied in our kinetic model. Firstly, the  $Y_{\text{X/COD}}$ , is identical in entire  $\gamma_{\text{COD}}$  range. Secondly, the microbial composition and viability of biomass is unchangeable. Thirdly, the  $\gamma_{\text{X}}$  in both digesters is constant, irrespective of  $q_{V}$ , which is achieved with biomass circulation. By considering Eq. (3) and the above assumptions, Eqs. (1) and (2) can be defined as follows:

$$\left(r_{\max}\gamma_{\text{COD},1}/\left(K_s + \gamma_{\text{COD},1}\right)\right) \exp\left(-\gamma_{\text{COD},1}/K_{\text{IA}}\right) = \left(q_V/V_1\right)\left(\gamma_{\text{COD},i} - \gamma_{\text{COD},1}\right) \tag{4}$$

thus with further algebraic manipulation  $V_1$  and  $V_2$  can be calculated by:

$$V_{1} = \left[ \left( r_{\text{max}} \gamma_{\text{COD},1} / \left( K_{s} + \gamma_{\text{COD},1} \right) \right) \exp \left( -\gamma_{\text{COD},1} / K_{\text{IA}} \right) \right]^{-1} q_{V} \left( \gamma_{\text{COD},i} - \gamma_{\text{COD},1} \right)$$
(6)

$$V_{2} = \left[ \left( r_{\text{max}} \gamma_{\text{COD},2} / \left( K_{s} + \gamma_{\text{COD},2} \right) \right) \exp \left( -\gamma_{\text{COD},2} / K_{\text{IA}} \right) \right]^{-1} q_{V} \left( \gamma_{\text{COD},1} - \gamma_{\text{COD},2} \right)$$
(7)

where:  $r_{\text{max}}$  – maximum degradation rate of COM. It is evident from Eqs. (4) and (5) that only  $\gamma_{\text{COD}}$  is functional depending upon  $q_V$ , meanwhile other parameters are

constant. Therefore, if the mass balance of COM in a steady state at various industrial wastewater dilution rates, D, is known, then parameters ( $r_{\text{max}}$ ,  $K_s$  and  $K_{\text{IA}}$ ) can be determined using non-linear fitting method. The D is defined as the quotient between  $q_V$  and V. Generally, in the case of COM inhibition presence, the curve  $-r_{\text{COD}} = f(\gamma_{\text{COD}})$  has a specific convex-shape. Consequently, such a curve has a maximum ( $dr_{\text{COD}}/d\gamma_{\text{COD}} = 0$ ) which, when considering Aiba's expression, follows the equation:

$$r_{\text{max}}\gamma_{\text{COD}}/(K_s + \gamma_{\text{COD}}) \left[ 1/\gamma_{\text{COD}} - 1/(K_s + \gamma_{\text{COD}}) - 1/K_{\text{IA}} \right] \exp(-\gamma_{\text{COD}}/K_{\text{IA}}) = 0 \quad (8)$$

According to the criterion for MTHT of two in series connected aerobic digesters (Levenspiel, 1999), the mathematical solution of Eq. (8) presents the value  $\gamma_{\text{COD},1}$  in Eqs. (6) and (7). Therefore, the optimal  $V_1$  and  $V_2$  for desired  $q_V$ ,  $\gamma_{\text{COD},i}$  and  $\gamma_{\text{COD},2}$ , can be calculated.

## 3. Experimental

The experiments performed in the laboratory W10 (Armfield) bench-top aerobic digester (V = 9 L) provided experimental data which were used for kinetic parameters' determination. The outflow  $\gamma_{\rm COD}$  versus  $q_V$  was measured. The  $q_V$  was varied from 0.001 to 0.0035 m³/d. Seven experiments were carried out. Initially, the digester was inoculated with 9 L of the aerobic biomass sludge, collected from an existing (municipal and industrial) full-scale aerobic wastewater treatment plant, and accustomized to its new environment by aeration at constant volume air flow rate ( $q_{V,a} = 1.6$  L/min) for a further 24 h. Thereupon, the aerobic digester was continuously started up using industrial wastewater at  $q_V = 0.001$  m³/d. It was operated at constant temperature,  $\theta = (25 \pm 1)$  °C during the experimental period. The outflow  $\gamma_{\rm COD}$  were daily determined. Furthermore, the  $\gamma_{\rm X}$  was also daily gravimetrically monitored during the operation and adjusted to the desired value ( $\gamma_{\rm X} = 5.0$  g/L), if required. The experiment was conducting until the steady-state conditions were established, i.e. until reaching constant outflow  $\gamma_{\rm COD}$ .

## 4. Results and discussion

The measured outflow  $\gamma_{\rm COD}$  under steady-state conditions at different  $q_V$ , are collected in Table 1. Corresponding D,  $-r_{\rm COD}$ , confidence intervals, CF, and wastewater treatment efficiencies as COD,  $\eta_{\rm COD}$ , were calculated. The  $-r_{\rm COD}$  is a product of D and the difference between  $\gamma_{\rm COD,i} = (5.10 \pm 0.10) \, {\rm kg/m^3}$  and  $\gamma_{\rm COD}$ .

Table 1: Experimental data in steady state at different  $q_V$ .

$q_{\nu}/(\mathrm{m}^3/\mathrm{d})$	D/(1/d)	$\gamma_{\rm COD}/({\rm kg/m}^3)$	$-r_{\text{COD}}/(\text{kg/(m}^3\text{ d}))$	CF/%	$\eta_{ m COD}$ /%
0.0010	$0.11 \pm 0.01$	$0.150 \pm 0.02$	$0.544 \pm 0.051$	9.3	$97.1 \pm 2.8$
0.0015	$0.17 \pm 0.01$	$0.240 \pm 0.02$	$0.826 \pm 0.052$	6.2	$95.3 \pm 2.7$
0.0020	$0.22 \pm 0.01$	$0.750 \pm 0.06$	$0.957 \pm 0.050$	5.3	$85.3 \pm 2.8$
0.0025	$0.28 \pm 0.01$	$1.240 \pm 0.06$	$1.081 \pm 0.051$	4.7	$76.7 \pm 2.7$
0.0030	$0.33 \pm 0.01$	$2.040 \pm 0.07$	$1.010 \pm 0.051$	5.0	$60.0 \pm 2.7$
0.0035	$0.38 \pm 0.01$	$3.600 \pm 0.08$	$0.570 \pm 0.051$	8.9	$29.4 \pm 2.6$

The aerobic biomass sludge removed more than 97 % of the COM presented in the industrial wastewater at D=0.11 (1/d) (sixth column in Table 1). Moreover, the UV spectrophotometric method (ISO 9648 1988-12-15, 1989) for chemical determination of tannins shoved again that mass fraction of plant tannins regarding overall COM in outflow remained almost the same as in the inflow ( $w_T=30$  %). Therefore, it can be concluded that biomass sludge from the existing wastewater treatment plant has a good degradation ability regarding plant tannins in industrial wastewater. However, the  $\eta_{\text{COD}}$  decreases steeply with increasing D. Variation in the  $-r_{\text{COD}}$ , with  $\gamma_{\text{COD}}$ , obtained from batch experiments, is shown in Fig. 2. The experimental data yielded the following Aiba's kinetic parameters' values:  $r_{\text{max}} = (1.87 \pm 0.38) \text{ kg/(m}^3 \text{ d})$ ;  $K_s = (0.32 \pm 0.12) \text{ kg/m}^3$ ;  $K_{\text{LA}} = (3.58 \pm 0.96) \text{ kg/m}^3$ .

In the second part of the research we calculated the optimal  $\gamma_{COD,1}$ , using the criterion of a MTHT of two in-series connected aerobic digesters. When considering experimentally-defined Aiba's inhibition kinetic parameters, a numerical solution of Eq. (8),  $\gamma_{COD,1} = 0.922 \text{ kg/m}^3$  was obtained. Therefore, the minimal volumes of the two inseries connected aerobic digesters (Eqs. (6) and (7)) for the degradation of wastewater from an industrial tannins production plant, can be calculated as follows:

$$V_1 = 0.932q_V \left( \gamma_{\text{COD}_1} - 0.922 \right) \tag{9}$$

$$V_2 = \left[ 1.87 \gamma_{\text{COD},2} / (0.32 + \gamma_{\text{COD},2}) \exp(\gamma_{\text{COD},2} / 3.58) \right]^{-1} q_V (0.922 - \gamma_{\text{COD},2})$$
 (10)

Wastewater treatment plant construction beside existing tannins production plant with  $q_V = 120 \text{ m}^3/\text{d}$  and  $\gamma_{\text{COD,i}} = 5.1 \text{ kg/m}^3$ , would require investment in two aerobic digesters with  $V_1 = 467 \text{ m}^3$  and  $V_2 = 228 \text{ m}^3$ , respectively. An outlet mass concentration of COM,  $\gamma_{\text{COD,2}} = 0.1 \text{ kg/m}^3$  is supposed. The total volume of both aerobic digesters is,  $V = 695 \text{ m}^3$ . However, this is appreciably less than the volume for only one aerobic digester ( $V = 1386 \text{ m}^3$ ) which is calculated by Eq. (6) when considering experimentally defined Aiba's inhibition kinetic parameters,  $q_V = 120 \text{ m}^3/\text{d}$ ,  $\gamma_{\text{COD,i}} = 5.1 \text{ kg/m}^3$ , and  $\gamma_{\text{COD,1}} = 0.1 \text{ kg/m}^3$ .

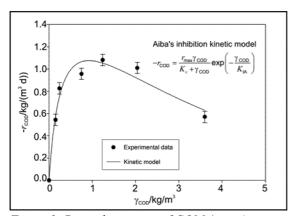


Figure 2: Degradation rate of COM  $(-r_{COD})$  vs. mass concentration of COM.

### 5. Conclusion

The kinetic parameters of the Aiba' inhibition kinetic model were successfully determined using the mass balance of COM data obtained from experiments in the laboratory bench top aerobic digester. Afterwards, we estimated the optimal volumes of two in series connected aerobic digesters using criterion of a MTHT. Technological and economical authorization for a two-stage wastewater treatment plant was mainly confirmed with a more than two times lower total digester volume compared to one-stage plant. Consequently, the importance of aerobic digesters' design using the criterion of a MTHT of two in-series connected digesters was proved.

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