Desalination and Water Treatment
www.deswater.com
29 (2011) 264–270
May
1944-3994 / 1944-3986 © 2011 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2011.2182

Biodegradation rate constants in different NF/UF fractions of cork processing wastewaters

Marisa Bernardo[a], Ana Santos[a], Paula Cantinho[a], Miguel Minhalma[a,b]*

[a]*Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa (ISEL/IPL), Rua Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal*
Tel. +351 218317178; Fax +351 218317267; email: bernardo_marisa@hotmail.com, anacatcs@gmail.com, pcantinho@deq.isel.ipl.pt, mminhalma@deq.isel.ipl.pt
[b]*Instituto de Ciência e Engenharia de Materiais e Superfícies (ICEMS/IST/UTL), Av. Rovisco Pais, 1, 1049-001 Lisboa, Portugal*

Received 29 July 2010; Accepted in revised form 16 December 2010

ABSTRACT

Cork processing wastewater is an aqueous complex mixture of organic compounds that have been extracted from cork planks during the boiling process. These compounds, such as polysaccharides and polyphenols, have different biodegradability rates, which depend not only on the nature of the compound but also on the size of the compound. The aim of this study is to determine the biochemical oxygen demands (BOD) and biodegradation rate constants (k) for different cork wastewater fractions with different organic matter characteristics. These wastewater fractions were obtained using membrane separation processes, namely nanofiltration (NF) and ultrafiltration (UF). The nanofiltration and ultrafiltration membranes molecular weight cut-offs (MWCO) ranged from 0.125 to 91 kDa. The results obtained showed that the biodegradation rate constant for the cork processing wastewater was around 0.3 d^{-1} and the k values for the permeates varied between 0.27–0.72 d^{-1}, being the lower values observed for permeates generated by the membranes with higher MWCO and the higher values observed for the permeates generated by the membranes with lower MWCO. These higher k values indicate that the biodegradable organic matter that is permeated by the membranes with tighter MWCO is more readily biodegradated.

Keywords: Cork processing wastewater, Fractionation, Membranes, Biochemical oxygen demand, Biodegradation rate constant

1. Introduction

The determination of BOD is one of the oldest and most established methods for assessing the content of biodegradable organic matter present in water [1–3].

BOD is usually defined as the amount of oxygen used by bacteria in the decomposition of organic matter under aerobic conditions. This happens due to the presence of a group of heterotrophic microorganisms that carry out oxidation, according to [5,6]:

$$\text{COHNS} + \text{O}_2 + \text{bacteria} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NH}_3 + \text{other end products} + \text{energy} \quad (1)$$

Theoretically, an infinite time is required for the complete biological oxidation of organic matter. However, for practical purpose, the reaction is usually considered to be complete in 20 days due to the oxidation of 99.9% of the biodegradable organic matter initially present [6].

* Corresponding author.

The kinetics of the biodegradation reaction is usually expressed as a first order reaction. This first order kinetics is very common due to its harmony with other physical processes related to BOD, such as, oxygen transfer from air to water [7] and self-purification capacity of streams [8], which also have first order kinetics characteristics.

In first order kinetics, the reaction rate is proportional to the amount of remaining organic matter over time. The reaction rate is controlled by the amount of organic matter available to microorganisms and can be expressed by [5]:

$$\frac{d\,\mathrm{BOD_r}}{dt} = -k\,\mathrm{BOD_r} \tag{2}$$

where BOD_r represents the concentration of the remaining organic matter after a period of time (t) and k the reaction rate constant in d^{-1}.

From the integration of Eq. (2) results:

$$\mathrm{BOD_r} = \mathrm{BOD_u}(e^{-kt}) \tag{3}$$

where BOD_u represents the ultimate concentration of biodegradable organic matter. Accordingly, the BOD_t measured in a period of time t, can be expressed by [5]:

$$\mathrm{BOD_t} = \mathrm{BOD_u} - \mathrm{BOD_r} \tag{4}$$

$$\mathrm{BOD_t} = \mathrm{BOD_u} - \mathrm{BOD_T}\left(e^{-kt}\right) \tag{5}$$

$$\mathrm{BOD_t} = \mathrm{BOD_u}\left(1 - e^{-kt}\right) \tag{6}$$

The value of the reaction rate constant (k) for a given water can be determined experimentally, or, for some waters, the value of this parameter is already established and is available in the literature [5,9]. For a given k, Eq. (6) allows the determination of the total BOD value of a water sample (BOD_u, BOD_{20}) from the value of BOD in any given period of time. There are several ways to determine these two parameters, k and BOD_u, from the results of a series of BOD measurements. The most common methods are the method of least squares, the method of moments [10], the daily difference method [11], the rapid rate method [12], the Thomas method [13] and the Fujimoto method [14].

The reaction rate constant, in Eq. (6), depends on the temperature but also on the type of organic matter present. So, for a given temperature, different values of k can be obtained due to the nature of organic matter and its availability to the microorganisms. In general, the organic matter that is dissolved is more readily available than the colloidal or suspended matter. In these cases, the rates of hydrolysis and diffusion are important factors in controlling the speed of reaction. In industrial wastewaters, organic matter may have a complex chemical nature. Simple substrates such as glucose are easily degraded, so k will be high. However, some organic compounds like lignin are slowly degraded by bacteria being often considered resistant to biodegradation and presenting a low k value [5,6].

The k value for untreated urban wastewater usually varies from 0.12 to 0.46 d^{-1} with a typical value of about 0.23 d^{-1}. However, the k value varies significantly with the nature of organic matter and values from 0.05 to 0.3 d^{-1} may be obtained for some industrial wastewaters [9].

Cork processing wastewaters are composed by different types of organic matter, including compounds that are hardly biodegradable, such as phenolic compounds, and this causes a major problem if biological treatments are envisaged for the treatment of these wastewaters. Previous studies have shown that the biodegradability (BOD_5/COD) of these wastewaters is low, 0.38, but this value can be increased using nanofiltration, where the permeates present BOD_5/COD values around 0.68 [15].

The aim of this study is to assess the k values for this wastewater and for different fractions obtained through ultra-nanofiltration membrane separation processes.

2. Materials and methods

2.1. Cork processing wastewater

Cork processing wastewater with different organic matter loads (generated after 20 t and 22 t of cork processed) were collected at Fabricor Indústria, Preparação e Transformação de Cortiça SA (Alcochete, Portugal). The boiling tank has a volume of 16 m^3.

2.2. Characterization of cork processing wastewater and permeated fractions

The cork processing wastewater was characterized in terms of pH, total organic carbon (TOC), biochemical oxygen demand (BOD_5 and BOD_{20}), chemical oxygen demand (COD) [16], total phenols (TP) [17] and tannins [18].

For the permeated fractions the BOD variation with time was recorded every day during a period of 20 days. BOD was determined according with the procedure described in the Standard Methods, by the respirometric method, 5210D. The biodegradation rate constant (k) was determined using the method of the least squares, considering Eq. (6) and the experimental BOD data obtained for each permeated fraction over a period of 20 days.

2.3. Preparation of ultrafiltration membranes

Six ultrafiltration membranes of cellulose acetate (designated by CA_0–CA_5) with different molecular weight cut-offs (MWCO) were prepared in the laboratory by the phase inversion method [19,20] using cellulose acetate with 40% acetyl content. Table 1 displays the casting solution composition and conditions for the preparation of CA_0–CA_5 membranes. All the chemicals used are of reagent grade and supplied by Merck.

Table 1
Membrane casting solutions composition and film casting conditions

Membranes	CA_0	CA_1	CA_2	CA_3	CA4	CA_5
Casting solution, wt%						
Cellulose acetate	17	17	17	17	17	17
Acetone	64	61	56	55	48	43
Formamide	19	22	27	28	35	40
Casting conditions						
Temperature of casting solution, °C	20–25	20–25	20–25	20–25	20–25	20–25
Evaporation time, min	0.5	0.5	0.5	0.5	0.5	0.5
Gelation medium	Water between 0–3°C					

2.4. Ultrafiltration and nanofiltration permeation experiments

Ultrafiltration and nanofiltration permeation experiments with cork processing wastewater were carried out on two different installations. The ultrafiltration installation consists in a feed tank with a volume of 5 L, a pump (with flow regulator), a flat sheet permeation cell, a pressure valve, 2 manometers (before and after a membrane cell), and a rotameter. The permeation cell holds 2 membranes with a surface area of 0.0147 m^2/membrane. The installation scheme is shown in Fig. 1 (left).

Nanofiltration experiments were carried out in a pilot plant equipped with a spiral wound membrane module DK20/40 GE (with a membrane surface area of 2.09 m^2). The installation consists in two pumps, two manometers, a rotameter and one microfiltration filter. The temperature of the feed tank (36 L) was kept constant by a cooling system (Fig. 1, right).

The permeation experiments were performed in total recirculation mode (with recirculation of both permeate and concentrate to the feed tank). For each membrane the same raw wastewater was used as feed solution and permeates were stored at 4°C for later analysis. The ultrafiltration experiments were performed with a volume of effluent of 5 L, at a transmembrane pressure of 3 bar, feed circulation flowrate of 200 L/h and 25°C. Nanofiltration experiments were performed with a volume of 20 L, at a transmembrane pressure of 10 bar, 25°C and a feed circulation flowrate of 500 L/h.

2.5. Membranes characterization

The ultra-nanofiltration membranes were characterized in terms of hydraulic permeability (L_p), apparent rejection coefficients to salts (f) and molecular weight cut-off (MWCO).

The hydraulic permeability was determined by performing water permeation experiments. For ultrafiltration, the experiments were carried out at transmembrane pressures of 1.0, 1.5, 2.0, 2.5 and 3.0 bar, at a feed circulation flowrate of 200 L/h, at a temperature of 25°C and using a surface area of membrane of 0.0294 m^2. For the nanofiltration, a DS5 commercial membrane supplied by GE was used and the transmembrane pressure was varied between 2.5 and 15.0 bar, at a temperature of 25°C and a feed circulation flowrate of 550 L/h, the surface area of membrane was of 2.09 m^2.

The determination of the apparent rejection coefficients to salts (f) was carried out with a monovalent salt, NaCl, and with a divalent salt, Na_2SO_4. For salt concen-

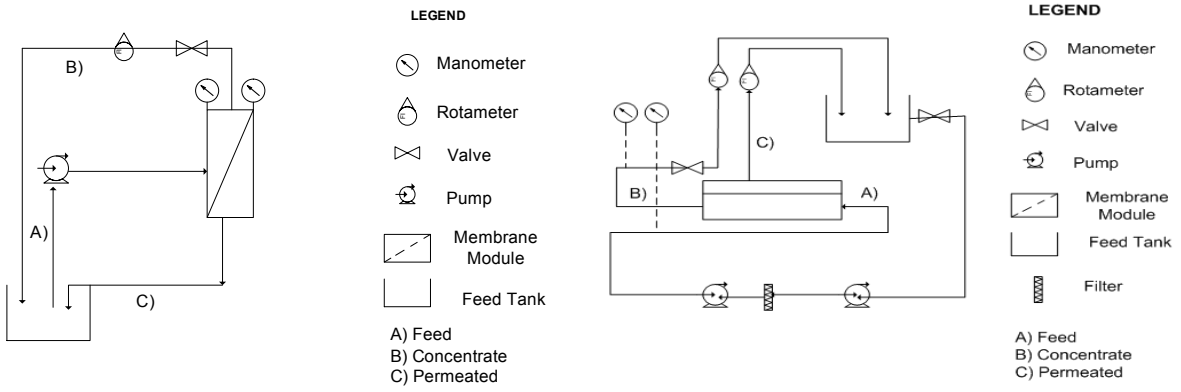

Fig. 1. Ultrafiltration (left) and nanofiltration (right) set-ups.

tration determination, conductivity measurements were performed using a WTW multi 340i/set and the apparent rejection coefficient was calculated according to the following equation: $f = (C_b - C_p)/C_b$, where C_b is the feed concentration and C_p is the permeate concentration. Ultrafiltration experiments were performed at a transmembrane pressure of 1 bar, temperature of 25°C, and a feed circulation flowrate of 200 L/h with salt concentrations of 600 ppm. Nanofiltration experiments were performed at a transmembrane pressure of 5 bar, temperature of 25°C, a feed circulation flowrate of 500 L/h with salt concentrations of 600 ppm.

The molecular weight cut-off (MWCO) determination was carried out following Michaels method, using different reference organic solutes with concentrations of 600 ppm. For the nanofiltration membrane, glucose and sucrose were used, and for the ultrafiltration membranes, polyethylene glycols of different molecular weights (600, 1000, 1500, 3000, 6000, 10000, 20000 Da) and dextrans (40000 and 70000 Da) were used. The ultrafiltration experiments were performed at a transmembrane pressure of 1 bar, temperature of 25°C, a feed circulation flowrate of 200 L/h. Nanofiltration experiments were performed at a transmembrane pressure of 5 bar, temperature of 25°C, a feed circulation flowrate of 550 L/h. The quantification of the concentration of the different organic solutes in the different streams (feed and permeate) was performed by analysis of the total organic carbon (TOC).

3. Results and discussion

3.1. Cork processing wastewater characterization

The wastewater characterization in terms of pH, total organic carbon (TOC), biochemical oxygen demand (BOD_5 and BOD_{20}), chemical oxygen demand (COD), total phenols (TP) and tannins for the two cork processing wastewaters samples is presented in Table 2.

Table 2 shows that this wastewater contains a high content in terms of organic matter, a considerable content in terms of polyphenols and tannins, that are generally difficult compounds to biodegrade, and a biodegradation ratio (BOD_5/COD) of 0.36, which is within the range of the typical values observed for urban wastewaters [5].

Table 2
Cork processing wastewater characterization. Samples collected after 20 and 22 tonnes of cork processed in the boiling stage

	Sample 1 (20 t of cork processed)	Sample 2 (22 t of cork processed)
pH	5.14	4.70
TOC (mg C/L)	670.5	1056.8
BOD_5 (mg O_2/L)	875	900
BOD_{20} (mg O_2/L)	1000	1225
COD (mg O_2/L)	2285	2604
TP (g tannic acid/L)	0.36	0.41
Tannins (g tannic acid/L)	0.25	0.27

The BOD variation with time for the two samples is displayed in Fig. 2.

The determination of the biodegradation rate constant for the wastewaters was carried out using the data presented in Fig. 2 and Eq. (6). The results are presented in Table 3.

The k values obtained for the two samples are very similar to each other and are within the range observed for untreated urban wastewater [5]. The estimated values for BOD (lines in Fig. 2) using the determined k values show a very good agreement with the experimental values. The average value of 0.3, obtained for k, together with the BOD_5/COD observed, around 0.36, indicates that the compounds present in these wastewaters are hardly/slowly biodegraded.

3.2. Membranes characterization

The membranes characterization results are shown in Table 4.

3.3. Membrane permeate fractions

Several permeation experiments with cork processing wastewater were carried out using the 7 membranes studied, with MWCOs ranging from 0.125 to 91 kDa. The wastewater samples used were collected after the processing of 20 and 22 t of cork, respectively, in a 16 m^3 boiling tank. The determination of the biodegradation

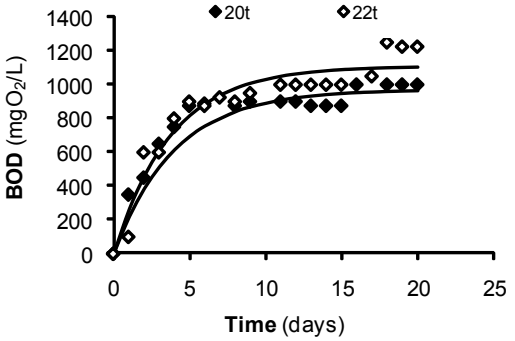

Fig. 2. Variation of the cork processing wastewater BOD with time. Samples collected after 20 and 22 tonnes of cork processed in the boiling stage.

Table 3
Cork processing wastewater biodegradation rate constant (k)

	20 t of cork processed	22 t of cork processed
k (d^{-1})	0.33	0.27

Table 4
Membranes characterization

	DS-5	CA_0	CA_1	CA_2	CA_3	CA_4	CA_5
L_p (L/h/m^2)	5.2	1.4	2.6	34.8	37.8	56.0	106.0
f (%) (NaCl)	60.0	40.0	30.6	2.0	0.8	0.4	0.1
f (%) (Na_2SO_4)	99.0	62.1	50.2	6.8	4.8	6.7	1.2
MWCO (kDa)	0.125	1.2	3.8	13.6	25	45	91

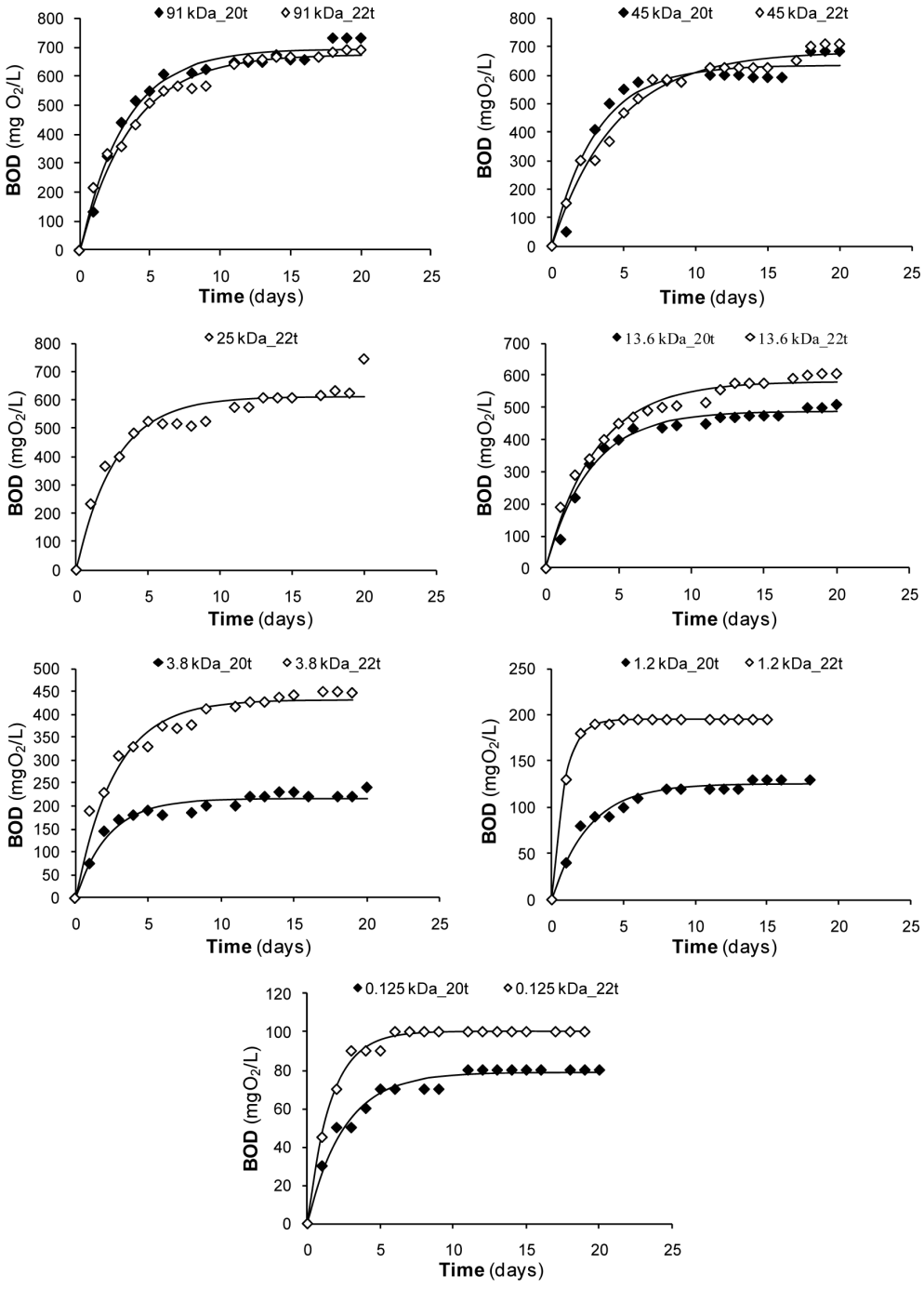

Fig. 3. Variation of permeates BOD with time for membranes with MWCO ranging from 0.125 kDa to 91 kDa.

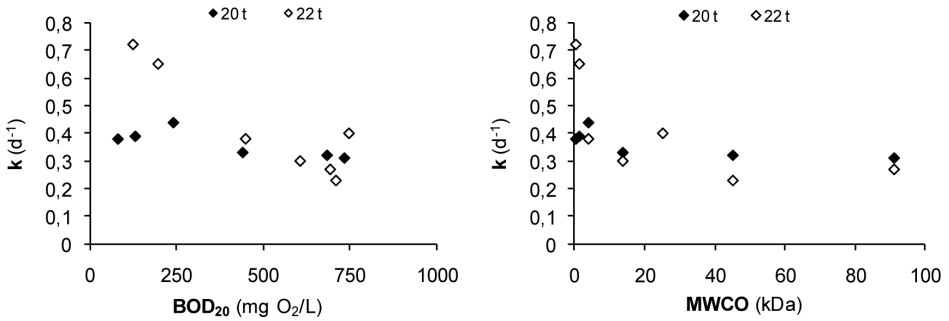

Fig. 4. Variation of biodegradation rate constant (k) with BOD_{20} and with MWCO.

rate constant (k) for the different permeates was carried out using the BOD vs. time data (presented in Fig. 3) and Eq. (6).

Fig. 4 shows the biodegradation rate constant (k) values, obtained for the different permeates, as a function of the MWCO (right) and as a function of the BOD_{20} (left).

The results obtained show that there is a significant increase of k with decreasing MWCO, for permeates generated by membranes with MWCO lower than 3.8 kDa, values in the range of 0.38–0.72 d^{-1} were obtained (being this phenomena more pronounced for the wastewater generated after 22 t of cork processed), which are much higher values than the ones observed for the raw wastewater (~0.3 d^{-1}). For the permeates obtained with membranes with higher MWCOs the k values tend to reach a plateau, with values around 0.3, being these values in the same range of the raw wastewater. These results suggest that the wastewater fractions obtained with lower MWCO membranes have permeated organic matter that is more readily biodegradable, which can be correlated with the fact that the solutes permeated are the ones with smaller molecular weights and therefore are more easily biodegraded. One other aspect is that there can also be present a toxicity/inhibition phenomenon that could be attributed to high concentrations of tannins [21]. The preceding analysis is in accordance with the results observed in Fig. 4 (left), showing that, in general, for lower values of BOD_{20}, higher values of k are obtained.

4. Conclusions

The complex nature of the cork processing wastewaters, rich in compounds that are hardly biodegradated, poses major problems in their treatment, namely if biological treatments are envisaged. The results obtained shown that the fractionation by nanofiltration and ultrafiltration permits to obtain wastewater fractions with different biodegradation rate constants. Higher values of k are observed for the permeate fractions generated by membranes with MWCO lower than 3.8 kDa, indicating that the biodegradable organic matter present in these permeates is more rapidly biodegradable. Therefore, if the wastewaters are pre-treated by ultrafiltration membranes with a MWCO lower than 3.8 kDa its discharge into municipal collectors is admissible and the subsequent biological treatments may present good efficiencies.

Acknowledgements

The authors acknowledge Fundação para a Ciência e Tecnologia (FCT) for financial support to the project PTDC/EQU-EQU/68424/2006 and the company Fabricor, Indústria, Preparação e Tranformação de Cortiças, SA for the wastewater samples.

References

[1] I. Karube, T. Matsunaga, S. Mitsuda and S. Suzuki, Microbial electrode BOD sensor, Biotechnol. Bioeng., 19 (1977) 1535–1547.
[2] L. Marsilli, Modelling batch BOD exertion curves, Environ. Technol. Lett., 7 (1986) 341–350.
[3] J. Marty, D. Olive and Y. Asano, Measurement of BOD: correlation between 5-day BOD and commercial BOD sensor values, Environ. Technol., 18 (1997) 333–337.
[4] Z. Yang, H. Suzzuki, I. Karube and S. Mcniven, Comparison of the dynamic transient and steady state measuring methods in a batch type BOD sensing system, Sens. Actuators B, 45 (1997) 217–222.
[5] Metcalf and Eddy, Wastewater Engineering Treatment and Reuse, 4th ed., McGraw Hill, London, 2003.
[6] C. Sawyer, P. McCarty and G. Parkin, Chemistry for Environmental Engineering, McGraw-Hill, London, 1994.
[7] W.C. Boyle, P.M. Berthouex and T.C. Rooney, Pitfall in parameter estimation for oxygen transfer data, J. Environ. Eng., 100 (1974) 391–408.
[8] E.B. Phelps, Stream Sanitation, John Wiley and Sons, New York, 1947.
[9] W.W. Eckenfelder, Industrial Water Pollution Control, 2nd ed., Mc Graw-Hill, London, 1989.
[10] E. Moore, A. Thomas and W. Snow, Simplified method for analysis of BOD data. Sewage Ind. Wastes, 22 (1950) 1343–1355.
[11] E.C. Tsivoglou, Oxygen Relationships in Streams, Sanitary Engineering Center, Technical Reports, W-58-2, Cincinnati, 1958.
[12] J.P. Sheehy, Rapid methods for solving monomolecular equations, J. Water Pollut. Control Fed., 32 (1960) 6.
[13] H. Thomas, Graphical determination of BOD curve constants, Water Sewage Works, 97 (1950) 123.
[14] Y. Fujimoto, Graphical use of first-stage BOD equation. J. Water Pollut. Control Fed., 36 (1961) 69–71.
[15] J. Oliveira, M. Nunes, P. Santos, P. Cantinho and M. Minhalma,

Cork processing wastewater treatment/valorisation by nanofiltration, Desal. Wat. Treat., 11 (2009) 224–228.
[16] APHA, AWWA, WPCF., Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington D.C., 1998.
[17] E.A. Ainsworth and K. Gilliespie, Estimation of total phenolic content and other oxidation substrates in plant tissues using Folin-Ciocalteu reagent, Nature. Protocols, 2 (2007) 875–877.
[18] H.P.S. Makkar, M. Blummel, M. Borowy and N.K. Becker, Gravimetric determination of tannins and their correlations with chemical and protein precipitation methods, J. Sci. Food Agric., 61 (1993) 161–165.
[19] B. Kunst and S. Sourirajan, An approach to the development of cellulose acetate ultrafiltration membranes, J. Appl. Polym. Sci., 18 (1974) 3423.
[20] M. Minhalma and M.N. de Pinho, Tannic-membrane interactions on ultrafiltration of cork processing wastewaters, Separ. Purif. Technol., 22–23 (2001) 479–488.
[21] J. Lin, W. Kao, K. Tsai and C. Chen, A novel algal toxicity testing technique for assessing the toxicity of both metallic and organic toxicants, Wat. Res., 39 (2005) 1869–1877.