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The effect of mixing pharmaceutical and tannery wastewaters on the biodegradation characteristics of the effluents

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Abstract

This paper evaluated the effect of mixing the effluent of a pharmaceutical plant producing acetylsalicylic acid with tannery wastewater, on the biodegradation of the effluents. The evaluation involved the analysis of the oxygen uptake rate (OUR), profiles of each wastewater and the mixture by respirometry. Model calibration using the experimental OUR data identified major COD fractions and associated process kinetics for all samples analyzed. The tannery sample was a plain-settled effluent having a total COD of around 2200 mg/L with a readily biodegradable fraction of 15%. The same fraction was 57% in the pharmaceutical wastewater sample having a much stronger total COD content of 40,435 mg/L. Consequently, mixing of the pharmaceutical effluent with the tannery wastewater up to 38% of the total COD in the mixture increased the readily biodegradable COD fraction but had an inhibitory effect on the biodegradation kinetics. This effect was relatively lower on growth, but quite significant on the hydrolysis of the slowly biodegradable COD decreasing the maximum hydrolysis rate from 2.0 day^{-1} to 1.2 day^{-1}. Model evaluation of the respirometric data, as performed in this study sets a workable protocol for the assessment of the compatibility of different wastewater mixtures for biological treatability.

Keywords: Acetylsalicylic acid effluent; COD fractions; Process kinetics; Respirometry; Tannery effluent

1. Introduction

This study is mainly focused on investigating changes likely to occur in the biodegradation kinetics of a mixture of two wastewaters with different characteristics. A practical concern about receiving a pharmaceutical effluent into a full-scale activated sludge plant originally built and operated for the treatment of tannery wastewater initiated the study. The adopted experimental approach was essentially based on the scientific understanding of complex substrate biodegradation established in the last two decades. In fact, until recent past, overall substrate parameters, such as biochemical oxygen demand, have been the major obstacle in the accurate assessment of biodegradation. Promotion of the chemical oxygen demand (COD) has been an improvement as the utilized COD could establish an electron balance with biomass generated and dissolved oxygen consumed but the problem of defining the entire substrate concentration with a single parameter still persisted [1]. Identification of COD fractions with different biodegradation characteristics was the expected major achievement in this field [2], which triggered the development of respirometry for COD fractionation and biodegradation kinetics [3,4]. This also led the way to multi-component models that incorporated COD fractionation and promoted the oxygen uptake rate (OUR), as the major parameter for wastewater characterization and process kinetics [5]. This approach provided a new insight to the biodegradation characteristics of domestic sewage [6–8]. It was successfully applied to different industrial wastewaters [9–11].

Pharmaceutical industry often generates high-strength wastewaters, changing in character and quantity depending upon the products and related manufacturing processes. Generally, pharmaceutical effluents are compatible with conventional biological treatment [12,13]. Rosen et al. [14] reported that biological treatment of chemical synthesis based pharmaceutical wastewater provided high COD removal and toxicity. No specific information is so far available in the literature on COD

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Nomenclature

b_H	endogenous decay rate (day^{-1})
C_{T1}	total influent COD (mgCOD/L)
f_a	activity coefficient (mgCOD/mgCOD)
f_{ES}	soluble residual fraction (mgCOD/mgCOD)
f_{EX}	particulate inert fraction (mgCOD/mgCOD)
k_h	maximum specific hydrolysis rates (day^{-1})
K_S	half-saturation coefficient (mgCOD/L)
K_X	half-saturation coefficients for hydrolysis (mgCOD/mgCOD)
OUR	oxygen uptake rate (mg/L h)
S_H	rapidly hydrolysable COD (mgCOD/L)
S_I	soluble inert COD (mgCOD/L)
S_O	oxygen concentration (mgO_2/L)
S_P	soluble residual COD generated as metabolic products (mgCOD/L)
S_S	readily biodegradable COD (mgCOD/L)
S_{T1}	influent soluble COD (mgCOD/L)
X_H	active heterotrophic biomass (mgCOD/L)
X_I	particulate inert COD (mgCOD/L)
X_P	particulate inert metabolic products (mgCOD/L)
X_S	slowly hydrolysable COD (mgCOD/L)
Y_H	yield coefficient (mgCOD/mgCOD)

Greek symbols

μ_H	maximum specific growth rate (day^{-1})

fractionation and biodegradation characteristics of acetylsalicylic acid production effluent.

Leather tanning generates a strong and complex wastewater, due to a sequence of processes involving high water use and an inflow of different type of chemicals. Tannery effluent is one of the most extensively studied industrial wastewaters, in terms of its characteristics [15], effect of specific pollutants such as chromium on treatability [16] and specific pretreatment requirements [17]. Based on the information presented in the literature, a plain-settled tannery wastewater, as used in this study, is expected to have a total COD content of around 2000–2500 mg/L, mostly of particulate nature enmeshed with chromium and other suspended pollutants. Studies on tannery effluent also set a good example for respirometric evaluation wastewater characteristics. Orhon et al. [18] indicate that in the plain-settled tannery wastewater, only 79% of the total COD is biodegradable, with 19% readily biodegradable and the remaining 60% slowly biodegradable COD both in the soluble and particulate range. The biodegradation kinetics of tannery wastewaters has been evaluated in a wide range of studies and the enhancement of biological treatment of tannery effluents has been one of the major concerns in these studies [19–21]

The objective of the study was to evaluate the effect exerted on the biodegradation characteristics of the effluents under aerobic conditions when the effluent of a pharmaceutical plant producing acetylsalicylic acid is mixed into plain-settled tannery wastewater. The evaluation was performed by generating and analyzing the specific oxygen uptake rate profiles of each wastewater and the mixture by respirometry. Model calibration using experimental OUR data identified biodegradation fingerprints, including major COD fractions and associated process kinetics for all samples analyzed.

2. Materials and methods

2.1. The survey sites

The study was conducted in the *Istanbul Organized Leather Tanning Industrial District*, located in Tuzla, Istanbul. The district presently houses around 110 tanneries processing both cattle hide and ship skin, resulting in an average total wastewater flow of around 12,000 m^3/day. In the district the entire combined wastewater is pretreated by plain settling prior to biological treatment by activated sludge. Recently, the district has served to a number of scientific studies focused on microbial ecology and system optimization for both organic carbon and nitrogen removal [22–24]. The study first involved a survey of 5 months on conventional characterization of the plain settling effluent fed to the activated sludge system. The results obtained, as outlined in Table 1, indicated that the biological treatment influent could be characterized by an average COD of 2170 mg/L with a soluble (filtered) fraction of 1070 mg/L, a total suspended solids (TSS), of 735 mg/L, a total sulfide of 70 mg/L and a total chromium of 35 mg/L, much the same as reported in earlier similar studies.

The pharmaceutical plant investigated in the study is an acetylsalicylic acid production facility, located near the *Istanbul Organized Leather Tanning Industrial District*. The production capacity is around 4500 kg/day in a batch wise operation during 6 days a week and 300 days a year. The wastewater flow generated from acetylsalicylic acid production is around 20–25 m^3/week with an average daily flow of 2.5 m^3. A similar survey on wastewater characteristics conducted on the plant for 3 months indicated that the process wastewater was quite strong with an average COD concentration of 40,300 mg/L, highly fluctuating in the range of 8000–76,000 mg/L. The wastewater

Table 1
Conventional characterization of the biological treatment influent at *Tuzla Organized Leather Tanning Industrial District*

Parameter	Unit	Value	Average
pH	–	6.9–8.7	7.4
TSS	mg/L	430–1080	735
Total COD	mg/L	1165–3000	2170
Filtered COD	mg/L	560–1915	1070
BOD_5	mg/L	500–1600	1110
TKN	mg/L	170–330	245
Filtered TKN	mg/L	112–282	195
NH_4–N	mg/L	73–210	130
S^{-2}	mg/L	10–145	70
Total Cr	mg/L	15–65	35
SO_4^{-2}	mg/L	1145–2345	1700
Cl^-	mg/L	4100–7130	5910
Alkalinity	mg/L	510–2200	1220
Oil & grease	mg/L	110–1475	355
Flowrate	m^3/day	2948–17,838	12,175