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Decoloration of textile wastewater by means of a fluidized-bed loop reactor and immobilized anaerobic bacteria

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Abstract

Textile wastewater was treated by means of a fluidized-bed loop reactor and immobilized anaerobic bacteria. The main target of this treatment was decoloration of the wastewater and transformation of the non-biodegradable azo-reactive dyes to the degradable, under aerobic biological conditions, aromatic amines. Special porous beads (Siran®) were utilized as the microbial carriers. Acetic acid solution, enriched with nutrients and trace elements, served both as a pH-regulator and as an external substrate for the growth of methanogenic bacteria. The above technique was firstly applied on synthetic wastewater (an aqueous solution of a mixture of different azo-reactive dyes). Hydraulic residence time was gradually decreased from 24 to 6 h over a period of 3 months. Full decoloration of the wastewater could be achieved even at such a low hydraulic residence time (6 h), while methane-rich biogas was also produced. The same technique was then applied on real textile wastewater with excellent results (full decoloration at a hydraulic residence time of 6 h). Furthermore, the effluent proved to be highly biodegradable by aerobic microbes (activated-sludge). Thus, the above-described anaerobic/aerobic biological technique seems to be a very attractive method for treating textile wastewater since it is cost-effective and environment-friendly.

Keywords: Acetic acid; Azo-reactive dyes; Anaerobic processes; Decoloration; Methanogenic bacteria; Textile wastewater

1. Introduction

Treating wastewater from cotton textile industries has become a real challenge the recent years. Different combinations of treatment methods have been proposed in order to effectively manage the above wastewater. Thus, chemical coagulation–flocculation, chemical oxidation, activated-carbon adsorption and anaerobic biological treatment, usually combined with a secondary activated-sludge treatment step, are among the most well known techniques [1–5].

Wastewater that results from the pre-treatment (desizing–scouring–bleaching) and dyeing processes of cotton fibers is generally characterized by its deep color, while in terms of organic content (COD) it is comparable to a moderate municipal wastewater [1,2]. The main problem that environmental engineers have to deal with is the elimination of the wastewater's color, which is due to the remaining dyes. The rejection of textile wastewater to the environment causes most of all aesthetic problems (the color change of a beautiful lake or river cannot be tolerated from the local communities). Also, the accumulation of color impedes sunlight penetration, disturbing thus the ecology of the receiving water [1–3]. Furthermore, several dyes and their decomposition derivatives have proved toxic to aquatic life (microorganisms, fish and mammals) [6–8].

"Azo-reactive" is probably the main class of textile dyes utilized for cotton fibers nowadays. They are complex organic compounds non-biodegradable by at least common aerobic microbes (activated-sludge) [9,10]. However, the above dyes decompose under highly reductive conditions leading to the formation of the so-called aromatic amines, which, in general, have proved degradable (under aerobic biological conditions) by numerous researchers over the recent years [11–15].

Anaerobic biological treatment methods, which provide a highly reductive environment and lead to the effective decomposition of azo-reactive dyes, are becoming increasingly important nowadays since they are cost-effective and environmentally safe. Anaerobic azo dye reduction has been studied intensively and is now well documented that it is a non-specific, microbial

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Nomenclature

COD	chemical oxygen demand (mg/L)
LLC	liquid level control
r_{acet}	acetic acid consumption rate ($g_{acet}\, m^{-3}_{reactor}\, day^{-1}$ or $g_{acet}/m^3_{wastewater}$)
R_{BG}	daily rate of biogas production ($m^3_{gas}\, m^{-3}_{reactor}\, day^{-1}$)
SEM	scanning electron microscope
SS	suspended solids (mg/L)
TS	total solids (mg/L)

Greek letters

λ_{max}	wavelength of the maximum absorbance in the visible spectrum region (nm)
τ	hydraulic residence time (h)

mediated and presumably extra-cellular process. Moreover, it is an enzymatic reaction, which involves reducing agents (e.g., riboflavin), acting as electron shuttles between the dyes and cellular-reducing enzymes [11–15].

The only disadvantage of the anaerobic biological techniques using conventional methods (e.g., stirred tank reactors) is the need for long hydraulic residence times and thus, the need for reactors of a high volume due to the low growth yields of the anaerobic bacteria (long generation times) [16,17]. However, the above disadvantage can be overcome by the utilization of methods and systems, which retain the biomass uncoupling and thus, hydraulic residence time from biomass accumulation (e.g., immobilization of microorganisms by colonization of a porous material) [18–20].

The objective of this work is the anaerobic biological treatment of textile wastewater using a bench-scale fluidized-bed loop reactor; special porous carriers and immobilized anaerobic bacteria (methanogens) are utilized. The high concentration of active microbial mass that can accumulate on the above carriers is expected to achieve wastewater decoloration at very low hydraulic residence times, decreasing thus substantially, both the capital and operational cost of textile wastewater treatment.

2. Materials and methods

2.1. Synthetic wastewater

The following three azo-reactive dyes, manufactured by DyStar (Germany), were dissolved in tap water at a concentration of 20 mg/L, each:

1. Remazol yellow RR (a mono-azo dye containing the vinylsulfonyl reactive group).
2. Remazol red RR (a mono-azo dye containing both the vinylsulfonyl and the monohalogentriazine reactive groups).
3. Remazol black B (a diazo dye containing two vinylsulfonyl reactive groups).

Also, 1 g/L $NaHCO_3$, 0.2–0.3 g/L NaOH and 0.5 g/L NaCl were utilized for the regulation of the wastewater's alkalinity (pH 8.5–9.0) and salinity, respectively. A few crystals of NaS were also added in the aqueous solution in order to remove dissolved oxygen. Moreover, three nutritious aqueous solutions, the compositions of which are presented in Table 1, were used in order to enrich the synthetic wastewater with the necessary, for microbial growth, nutrients and trace elements. All the above chemicals were provided by Fischer Scientific.

The above synthetic wastewater had an intensive red-reddish color and presented the highest absorbance peak (λ_{max}) in the visible spectrum region, at 550 nm.

2.2. Real textile wastewater

Textile wastewater was periodically withdrawn (during a 6-month period) from a nearby industry (in Xanthi, northeastern Greece). The above industry processes cotton and cotton–polyester textiles using almost exclusively azo-reactive

Table 1
Composition of the three nutritious aqueous solutions

Nutritious solution	Components	Concentration (g/L)
Aqueous solution I (N–P–S) (20 mL/L of wastewater)	NH_4Cl	114.6
	K_2HPO_4	33.7
	$(NH_4)_2SO_4$	16.5
Aqueous solution II (Ca–Mg) (2–3 mL/L of wastewater)	$CaCl_2{\cdot}2H_2O$	36.7
	$MgCl_2{\cdot}6H_2O$	41.8
Aqueous solution III (trace elements) (2 mL/L of wastewater)	$(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$	70.2
	$CuCl_2{\cdot}6H_2O$	0.54
	$ZnCl_2$	0.83
	$MnCl_2{\cdot}6H_2O$	0.72
	$NiCl_2{\cdot}6H_2O$	0.57
	$CoCl_2{\cdot}6H_2O$	0.16
	Na_2SeO_3	0.31
	H_3BO_3	0.57
	$Na_2MoO_4{\cdot}2H_2O$	0.01
	Regulation of pH < 2 utilizing HCl solution	

Table 2
Real textile wastewater characteristics

Samples	pH	TS (mg/L)	SS (mg/L)	COD (mg/L)
Sample-1	9.5	3760	15	400
Sample-2	8.5	2600	<10	415
Sample-3	8.5	680	<10	826
Sample-4	7.5	1520	<10	645
Sample-5	8.3	860	<10	430
Sample-6	8	885	<10	480
Mean value	8.4	1718	<10	532

and azo-disperse dyes for the dyeing of cellulosic and polyester fibers, respectively. The wastewater was constantly slightly alkaline and it was characterized by its deep color. Furthermore, the organic content (in terms of COD) was comparable to that of a moderate sewerage, while the concentration of total solids (TS) was relatively high due to the elevated concentration of dissolved salts (Table 2).

All the textile wastewater samples (Table 2) were enriched with the necessary, for microbial growth, nutrients and trace elements by the addition of the three nutritious aqueous solutions (Table 1).

2.3. The porous carriers

Three-dimensional colonization of anaerobic microbes was achieved by the use of spherical (diameter = 1–2 mm) reticulated sinter glass carriers (Siran®) manufactured by Schott Glaswerke (Germany). The manufacturing material was obtained by sintering a mixture of glass and sodium chloride powder followed by a washing process to eliminate the non-sinterable salt. The resulting reticulated glass sponge has a well-defined pore size distribution depending on the grain size of the salt; porosity is correspondingly a function of the percentage of the filling material. The sponge was then further processed to form spherical beads. The latter carriers (beads) have a porosity of 55% and a pore diameter range of 60–300 μm.

The microbial mass was immobilized by simply immersing the porous carriers into sludge that was withdrawn from the anaerobic digester of a municipal wastewater treatment plant. Anaerobic bacteria (e.g., methanogens) with a high affinity to adsorb on special surfaces (e.g., Siran®) create colonies in just a few minutes of time. Highly dense microbial mass and very short start-up time intervals can be achieved by the use of those carriers [19]. An SEM image of a sinter glass carrier is given in Fig. 1.

2.4. Fluidized-bed loop reactor

A glass-made fluidized-bed loop reactor of a total volume of 2 L and an internal diameter of 15 cm was utilized, while 60% of the reactor's total volume was filled with the above-mentioned porous carriers (Fig. 1). Temperature was maintained constant at 37 ± 1 °C by means of an external water-coil and a water-bath, while the pH was regulated within 6.4–7.2 using an acetic acid aqueous solution (CH_3COOH, 10%, v/v) and a pH-controller.

Fig. 1. SEM image of a sinter glass carrier (Siran®).

Peristaltic pumps were used for wastewater transportation and recycling, while recycling-flow to in-flow ratio was always kept over 20:1, simulating thus a complete-mixed continuous-flow reactor [21]. A liquid level control (LLC) system equipped with two electrodes (one of which continuously dipped in the liquid phase), connected to the out-flow pump, maintained the level of the liquid phase in the upper part of the reactor at a certain level; this way, the biogas accumulates on the top of the reactor. Biogas production rate (R_{BG}) was then calculated by means of a gas flow meter. Fig. 2 presents the flowsheet of the reactor.

2.5. Analytical methods

The absorbance spectrums at 400–800 nm were taken in order to calculate the intensity of wastewater's color, using a spec-

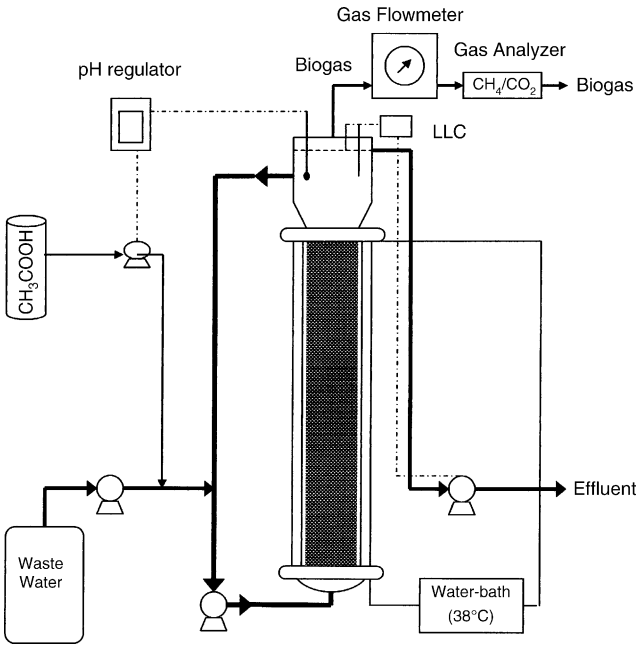

Fig. 2. Flowsheet of the fluidized-bed loop reactor.

trophotometer (WTW, Photolab Spektral); the samples were filtrated utilizing 0.2 μm pore filters prior to spectrophotometric analysis. The absorbance at 550 nm was taken as color intensity for the synthetic wastewater, while the mean values of the absorbance measurements at 436 nm (yellow region), 525 nm (red region) and 620 nm (blue region) were taken for real textile wastewater.

Chemical oxygen demand (COD) was measured using the open-reflux method [22]. Due to the colored samples, titration with ferrous ammonium sulfate using ferroin as the end-point indicator was preferred over photometric analysis [22].

Acetic acid concentration in the out-flow samples was determined using Gas Chromatography (Auto System XL Gas Chromatograph, Perkin-Elmer Instruments); the samples were filtrated utilizing 0.2 μm pore filters prior to the analysis.

The concentrations of methane (CH_4) and carbon dioxide (CO_2) in the biogas were continuously measured using an online gas-analyzer (BINOS IR, Leybold-Heraeus).

Traces of hydrogen sulfide (H_2S) in the biogas were determined regularly using the special Drager H_2S-analytical tubes (H_2S 0.2%/A;; CH 28101).

3. Results and discussion

3.1. Synthetic wastewater

Following the inoculation of the porous carriers, a start-up period of 2 weeks was necessary for the efficient growth of an active anaerobic biomass and the development of highly reductive conditions in the fluidized-bed loop reactor. During the above period of time, the reactor was continuously fed with synthetic wastewater, while hydraulic residence time was set to 24 h.

Samples of both the influent and effluent of the reactor were taken regularly after the start-up period for determination of color intensity. The decoloration of the wastewater (decoloration efficiency of 75%) was indicative of the anaerobic process that was developed in the reactor during the first 2 weeks (start-up period) of the experimental run (Fig. 3). The continuous growth of the microbial mass on the porous carriers due to the regular supply of acetic acid led to a decoloration efficiency of over 90% in the next 15 days (Fig. 3).

The inflow rate was then increased in order to set the hydraulic residence time to 18 h. As expected, a decrease in the decoloration efficiency was observed initially. However, and because of the continuous growth of anaerobic biomass on the porous carriers, decoloration efficiency reached 92% in the next 1 month. Likewise, hydraulic residence time was gradually decreased to only 6 h in the next 45 days of experimental run. As depicted in Fig. 3, each time hydraulic residence time was decreased; a drop in wastewater's decoloration efficiency was observed. However, the system retained high decoloration efficiency (over 90%) after a certain period of time due to the continuous development and increase of the anaerobic biomass on the porous carriers.

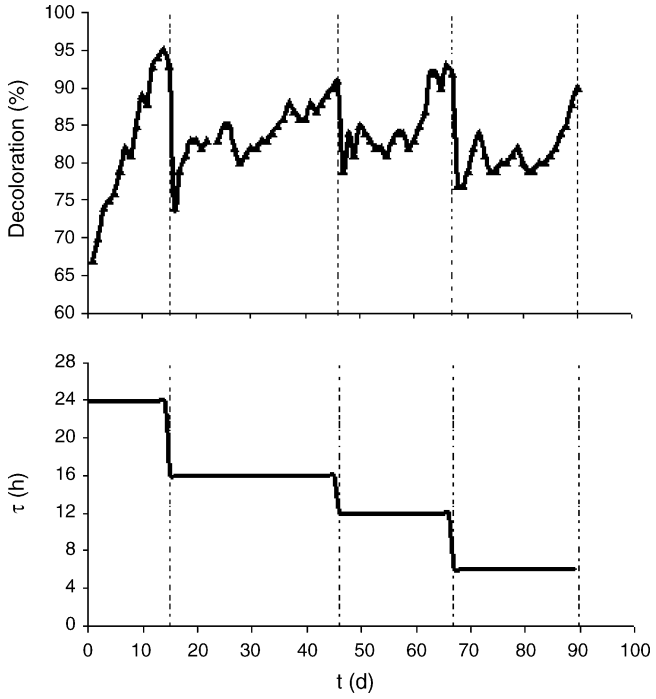

Fig. 3. Decoloration efficiency (%) of synthetic wastewater with time (days) at different hydraulic residence times (hours).

3.2. Textile wastewater

The synthetic wastewater was replaced by real textile wastewater (Table 2) 3 months after the start-up period continuing the experimental run at the above hydraulic residence time ($\tau = 6$ h). The initial drop in wastewater's decoloration efficiency can be attributed to the microbial shock due to the change of environment and the possible toxic or inhibitory effects of certain compounds of the textile wastewater on the microbes (Fig. 4).

Nevertheless, after an acclimatization period of 15 days, the anaerobic microbes retained their activity leading to a wastewater's decoloration efficiency of 90% (Fig. 4). Likewise, a small drop in decoloration efficiency was observed each time a new sample of textile wastewater was treated. The efficiency was though retained at its initial high level (almost complete decoloration) after a short acclimatization period of time (Fig. 4). Moreover, acetic acid consumption rate and biogas production

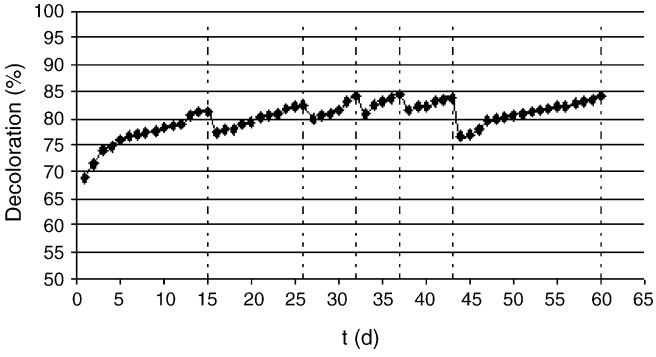

Fig. 4. Decoloration efficiency (%) of real textile wastewater with time (days) ($\tau = 6$ h).

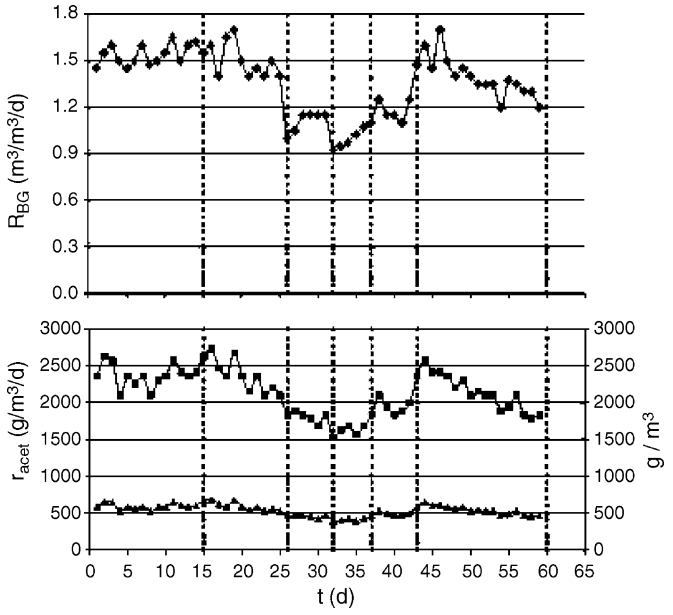

Fig. 5. Biogas daily production rate (R_{BG}) and acetic acid consumption rate (r_{acet}: (■) $g_{acet}\ m^{-3}_{reactor}\ day^{-1}$ and (▲) $g_{acet}/m^3_{wastewater}$) with time (days).

rate were stabilized in the region of around 2000 g/(m^3 day) (or 500 g/m^3 of wastewater) and 12–15 m^3/(m^3 day), respectively, as presented in Fig. 5.

The COD of the effluent was at all times almost equal to the COD of the untreated textile wastewater (Table 2). Furthermore, the effluent presented a high biodegradation affinity (by aerobic bacteria) as revealed by the utilization of a special microbial sensor [8]. These results agree with previous experiments during which, a series of two fixed-bed reactors at a pilot-plant scale and similar filling material (cylindrical rings made of Siran®) were utilized [20]. It is evident that the anaerobically treated textile wastewater can be safely treated then in a secondary activated-sludge treatment plant. Thus, the above combination of anaerobic/aerobic treatment can prove a very efficient method (both environmentally and economically) for the integrated management of textile wastewater.

Also, compared with the above previous experiments [20], the fluidized-bed loop reactor (Fig. 2) presented a slightly lower efficiency in terms of wastewater decoloration versus hydraulic residence time. The higher efficiency though of the pilot-plant unit can be, at least partially, attributed to the higher acclimatization period of time (the experiments were running continuously for 10 months utilizing real textile wastewater) [20].

3.3. Biogas composition

As Table 3 presents, the biogas produced during the whole experimental run was very rich in methane, while hydrogen sulfide was only present in traces. Although textile wastewater is generally rich in sulfate content (due to the dyestuff and the processing chemicals utilized), and the production of hydrogen sulfide thermodynamically favored over methane production (reactions (1) and (2)) [16,17], methanogens prevailed over sulfate reducers.

Table 3
Biogas composition (%)

CH_4	CO_2	H_2S
70–80	20–30	0.1–1

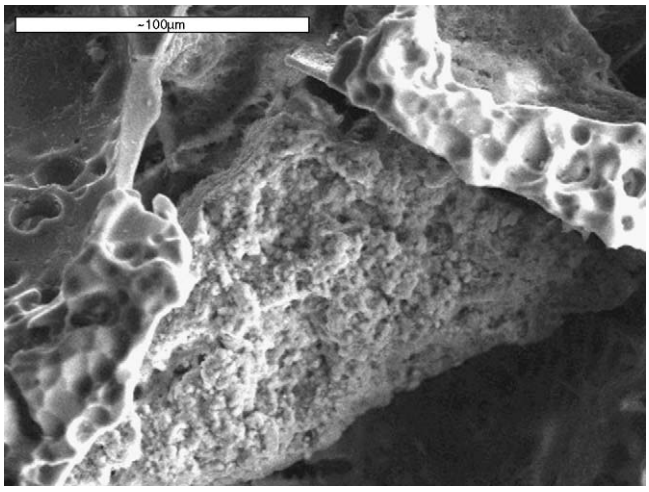

Fig. 6. SEM photo of a colony of methanogenic bacteria adsorbed on the inner area of a porous carrier (Siran®).

$$CH_3COOH \rightarrow CH_4 + CO_2,$$
$$\Delta G^{\circ\prime} = -31\ kJ/mol\ CH_3COOH \quad (1)$$

$$CH_3COOH + SO_4^{2-} + 3H^+ \rightarrow 2CO_2 + H_2S + 2H_2O,$$
$$\Delta G^{\circ\prime} = -63\ kJ/mol\ CH_3COOH \quad (2)$$

The above finding agrees with previous research works supporting the fact that the utilization of a porous material that acts as colonization media favors, in a high extent, the methanogenic bacteria over the sulfate reducing ones [23–25].

Fig. 6 presents an SEM photo of a microbial community (methanogenic bacteria) colonized on a certain inner area of a porous carrier. It is evident, also from the above photo, that methanogens have the affinity to adsorb and form colonies on this kind of filling material (Siran®).

4. Conclusions

Textile wastewater was treated utilizing a bench-scale fluidized-bed loop reactor with porous carriers colonized by anaerobic bacteria. Acetic acid solution (enriched with nutrients and trace elements) was used both as a pH-regulator and as an external substrate addition for the growth of methanogenic bacteria. The main aim of the treatment was decoloration of the textile wastewater and transformation of the non-biodegradable azo-reactive dyes to the degradable, under aerobic biological conditions, aromatic amines.

The above process method is very efficient since it is able to decolorize textile wastewater at very low hydraulic residence times (e.g., 6 h), while rich-in-methane biogas is also produced. Furthermore, the effluent presents high biodegradability by aero-

bic bacteria (activated-sludge). Thus, the above combination of anaerobic/aerobic treatment proves to be both a cost-effective and an environment-friendly technique.

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References

[1] U. Rott, R. Minke, Overview of wastewater treatment and recycling in the textile processing industry, Water Sci. Technol. 40 (1) (1999) 137–144.
[2] L.M. Shelley, W.C. Randall, H.P. King, Evaluation of chemical–biological and chemical–physical treatment for textile dyeing and finishing waste, Water Pollut. Control. Fed. 48 (4) (1976) 753–761.
[3] D. Georgiou, A. Aivasidis, J. Hatiras, K. Gimouhopoulos, Treatment of cotton textile wastewater using lime and ferrous sulfate, Water Res. 37 (9) (2003) 2248–2250.
[4] L. Nicolet, U. Rott, Recirculation of powdered activated carbon for the adsorption of dyes in municipal wastewater treatment plants, Water Sci. Technol. 40 (1) (1999) 191–198.
[5] R. Venkatandri, W.R. Peters, Chemical oxidation technologies: ultraviolet light/hydrogen peroxide, Fenton's reagent, and titanium dioxide-assisted photocatalysis, Hazard. Waste Hazard. Mater. 10 (2) (1993) 107–149.
[6] V.B. Ivanov, Reactive Dyes in Biology, Soviet Scientific Reviews, Harwood Academic Publishers, 1987.
[7] D. Brown, H.R. Hitz, L. Schafer, The assessment of the possible inhibitory effect of dye-stuffs on aerobic waste-water bacteria, experience with a screening test, Chemosphere 10 (3) (1981) 245–261.
[8] D. Georgiou, P. Melidis, A. Aivasidis, Use of a microbial sensor: inhibition effect of azo-reactive dyes on activated sludge, Bioprocess. Biosyst. Eng. 25 (2) (2002) 79–83.
[9] D.R. Waring, Dyes for cellulosic fibers, in: The Chemistry and Application of Dyes, Plenum Press, New York, 1990, p. 49.
[10] H.L. Needles, Color, dyes, dyeing and printing, in: Textile Fibers, Dyes, Finishes and Processes: A Concise Guide, Noyes Publications, 1986, p. 158.
[11] W. Delee, C. O'Neill, F.R. Hawkes, H.M. Pinheiro, Anaerobic treatment of textile effluents: a review, J. Chem. Technol. Biotechnol. 73 (1998) 323–335.
[12] D. Georgiou, C. Metallinou, A. Aivasidis, E. Voudrias, K. Gimouhopoulos, Decolorization of azo-reactive dyes and cotton-textile wastewater using anaerobic digestion and acetate-consuming bacteria, Biochem. Eng. J. 19 (2004) 75–79.
[13] M. Kudlich, P.L. Bishop, H.-J. Knackmuss, A. Stolz, Simultaneous anaerobic and aerobic degradation of the sulfonated azo dye Mordant Yellow 3 by immobilized cells from a naphatlenesulfonate-degrading mixed culture, Appl. Microbiol. Biotechnol. 46 (1996) 597–603.
[14] C. O'Neill, F.R. Hawkes, D.L. Hawkes, S. Esteves, S.J. Wilcox, Anaerobic/aerobic biotreatment of simulated textile effluent containing varied ratios of starch and azo dye, Water Res. 34 (8) (2000) 2355–2361.
[15] D.T. Sponza, M. Isik, Decolorization and azo dye degradation by anaerobic/aerobic sequential process, Enzyme Microb. Technol. 31 (2002) 102–110.
[16] J.G. Zeikus, Microbial populations in digesters, in: Anaerobic Digestion, Applied Science Publishers Ltd., London, 1979, pp. 61–87.
[17] G. Gottschalk, Bacterial Metabolism, second ed., Springer-Verlag Inc., New York, 1986.
[18] A. Aivasidis, C. Wandrey, Recent developments in process and reactor design for anaerobic wastewater treatment, Water Sci. Technol. 20 (1) (1988) 211–218.
[19] A. Aivasidis, Process development for anaerobic wastewater treatment using porous carriers for microbial colonization, Bioprocess. Eng. 4 (1989) 19–25.
[20] D. Georgiou, J. Hatiras, A. Aivasidis, Microbial immobilization in a two-stage fixed-bed-reactor pilot plant for on-site anaerobic decolorization of textile wastewater, Enzyme Microb. Technol. 37 (6) (2005) 597–605.
[21] O. Levenspiel, Chemical Reaction Engineering, second ed., Wiley Eastern Ltd., London, 1972.
[22] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 20th ed., 1998, pp. 5–13.
[23] Z. Isa, S. Grusenmeyer, W. Verstraete, Sulfate reduction relative to methane production in high-rate anaerobic digestion: microbiological aspects, Appl. Environ. Microbiol. (March) (1986) 580–587.
[24] Z. Isa, S. Grusenmeyer, W. Verstraete, Sulfate reduction relative to methane production in high-rate anaerobic digestion: technical aspects, Appl. Environ. Microbiol. (March) (1986) 572–579.
[25] F. Widdel, Microbiology and ecology of sulphate and sulphur-reducing bacteria, in: Biology of Anaerobic Microorganisms, Wiley and Sons, New York, 1988, pp. 459–586.