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Biological Removal of Impurities from Textile Industry Wastewaters: An Assessment

Abstract
Textile wastewaters (WW) contain specific impurities that impede their biological treatment. Thus, to be treated biologically, they require technological pre-treatment, mostly composition equalisation and neutralisation. If biological oxygen demand (BOD) is determined in WW, a biodegradation test may be used to determine whether biological treatment is possible. The phenomenon may be described mathematically, provided that the removal of impurities occurs in a homogenous velocity field. The functional relationships of the biodegradation process and continuous pollution removal in overflow tanks are described, and changes in chemical oxygen demand (COD) concentration and permanganate value (PV) occurring in cotton industry WW treatment are discussed.

Key words: *textile industry water wastes, biodegradation, activated sludge.*

Introduction

Biological treatment of textile industry wastewaters (WW) is used only exceptionally, mostly when biological oxygen demand for five days (BOD_5) must be decreased and the reduction level exceeds 60%. It is also advisable to add at least 50% of municipal sewage to textile industry WW. However, it should be notid that despite such precautions, operational difficulties caused by the uneven flow of loads of specific impurities (including toxic pollutants) which are not normally encountered in municipal sewage treatment must be overcome. Additionally, textile industry WW are characterised by a great variability of composition, which results not only from the multiphase nature of most technological processes but also from the chemicals used and the composition of the processed textile raw materials.

Reluctance to use biological textile WW treatment is also brought about by the fact that, apart from some wool industry WW and WW from preliminary treatment of natural silk, these wastes are considered to be poor in organic, biogenic compounds. However, if BOD_5 is used as an indicator of the WW biogenic impurity concentration, then the mean concentration of this type of WW is mostly comparable with that of municipal sewage. The ratio between BOD_5 and the total concentration of organic pollution is a different criterion, and rather unfavourable. Volatile substance content may be a general indicator of organic substance concentration, easy to determine analytically in this WW type. It may range between 30 and 40% of the dry residue indicator in textile WW, and even up to 70% of the indicator in WW from wool laundries. The volatile substance content in total solids in typical municipal sewage equals about 47%.

WW composition in cotton plants, as well as in the production and finishing of fabrics made from synthetic fibres, is least favourable for biological treatment. Unfortunately, at the beginning of the 21st century these plants are particularly important because of the production size and the volume of water used. Other branches, including the wool industry, also process considerable amounts of synthetic raw materials. As a result, the qualitative composition of textile WW has become considerably homogenised.

The aim of this paper is to examine the biological treatment of textile WW on the basis of a biodegradation test and its mathematical interpretation. The mathematical description of the process offered by the author includes the participation of the water environment in which biochemical changes to the organic substrate take place. The importance of the velocity field generated by micro-organisms during the transport of the adapted substrate structures to biochemical reaction centres is also emphasised.

Pollution Degree of Textile Wastewater

Textile plants continue to be a source of specific environmental pollution because of considerable amounts of mineral substances (mostly simple salts but also complex organic compounds) that are used to process textile raw materials and semi-finished products. Wet treatment processes influence WW salinity and organic pollution indicators, such as COD (chemical oxygen demand), TOC (total organic carbon), detergents or colour.

Industrial WW from extensive production cycles is characterised by a more balanced composition than those from small plants. Individual technological procedures, especially dyeing, washing, bleaching and finishing, have a particular impact on the WW composition in small plants.

In keeping with the traditional division of textile branches used in Poland, qualitative WW composition may range widely. WW quality parameters are given in Table 1 [1].

For the purposes of biological treatment of textile WW, biodegradable properties of organic pollution in treated wastes should be determined. The ratio between BOD_5, or possibly COD or permanganate value (PV) and the values of the volatile substances mentioned above, may be used as a preliminary criterion.

***Table 1.** Textile industry quality determinants - ranges [1].*

Parameter	Unit	WW composition in the following industries					
		cotton	wool	silk	knitting	flax	combed yarn
pH	-	5-140	4.0-9.5	3.7-9.5	4.0-11.0	3.0-11.2	6.0-8.8
Alkalinity	mval/dm^3	5-140	0-40	0-40	0-120	0-120	0-40
COD_{Mn}	mg O_2/dm^3	80-900	70-650	40-550	30-700	60-3900	100-2800
BOD_5	mg O_2/dm^3	50-700	30-450	30-700	30-650	30-1800	60-4000
COD_{Cr}	mg O_2/dm^3	100-1100	50-850	60-2800	60-1000	50-3600	50-2900
Chlorides	mg Cl/dm^3	60-650	50-600	40-1200	30-1800	30-300	100-300
Sulphates	mg SO_4/dm^3	50-750	50-450	50-540	30-450	35-180	100-1000
Detergents	mg/dm^3	1-70	5-100	4-35	0-120	-	5-120
Total dissolved solids	mg/dm^3	80-3600	50-2700	40-2900	40-2900	200-1900	400-1200
Total suspended solids	mg/dm^3	50-500	60-400	40-400	50-600	50-800	50-2400
Temperature	°C	30-60	25-50	35-700	35-60	25-65	20-50
Colour test	solution degree	1:10-1:700	1:10-1:550	1:8-1:400	3:5-1:400	1:2-1:200	1:10-1:300

The main load of organic impurities in textile WW, almost equivalent to the volatile substance mass, comes from the dyes used, as well as (sometimes) from finishing agents. They are products of chemical synthesis whose composition is often unidentified and even protected by the manufacturer. Their removal and decomposition in chemical and biological treatment processes are particularly difficult and pose the greatest problem.

Only some products of hydrolysis of fibre-forming substance from natural raw materials are biologically degradable. As the present author's analysis shows, the loss of the mass of fibre-forming raw material that undergoes hydrolysis in finishing processes is as follows:

- animal fibres (wool) 2-3 %; approximate statistical formula: $C_{21}H_3O_{15}N_6S$
- natural silk 36-42 %; approximate statistical formula: $C_3H_7O_3N$
- cotton fibres 1-3.3 %; approximate statistical formula: $C_6H_7O_2(OH)_3$
- flax fibres 17-20 %; approximate statistical formula: $C_{10}H_{12}O_2$

The loss of the mass of synthetic fibre raw material usually does not exceed 1%. However, these products are sparingly soluble in water, but solve well in concentrated alkalis. As the comparative analysis of WW qualitative composition demonstrates, textile WW parameters are fairly suitable for biological treatment, approaching those of municipal sewage. In the case of municipal wastewaters, it is generally accepted that the ratio BOD_5/organic substance of total solids equals 1:1.5 (300:450 - for sewage with average concentration) [2].

Prerequisites for Textile WW Biological Treatment

The biological treatment of textile WW depends on the preliminary technological processing of WW, which in turn facilitates the most important procedure, i.e. the biochemical adaptation of pollution in the final stage.

As studies on textile WW treatment conducted under the supervision of the present author at the Technical University of Łódź demonstrate, similarly to municipal and domestic sewage treatment, floating matter, including specific fibrous impurities, must first be removed. This is particularly necessary before the neutralisation process is conducted, if saturation with stack gases is used. Precipitates which form as a result of saturation (mostly carbonates and bicarbonates, together with fibres) produce felt-like crystallising settlings that impede the appropriate operation of the neutralisation equipment.

Neutralisation is required in cotton industry plants with the full production cycle, where bleachers are used, as well as in bleacheries of artificial fibres. WW from dyeing shops in which sulphur dyes are used may be alkaline; however, when mixed with other technological baths, this WW type does not require separate neutralisation.

Fine fibres are inevitably present in WW, even if filtration membranes are used. Fibrous impurities do not obstruct biological treatment, and are sometimes even helpful, provided that their amount and form are not indicative of wasteful usage of raw materials.

WW qualitative composition equalisation is another prerequisite for the biological treatment of textile WW [3]. As pollution concentrations vary greatly, the application of efficient and suitable tanks to equalise WW qualitative composition ensures a steady operation of the biological equipment. Additionally, it is also necessary to separate WW into concentrated WW and so-called washery effluent.

An excessive reaction connected with the presence of alkalis (mostly sodium hydroxide and sodium sulphide, as well as reactive dyes and detergents) impedes direct biological treatment of concentrated WW. Attempts to treat concentrated WW biologically, even after its equalisation, usually fail because of the factors given above. Excessive alkalinity hinders the respiratory processes. This is also true to a smaller degree of dyes and surfactants (detergents). In the case of cotton industry WW, the adaptation of activated sludge micro-organisms to their environment is possible as long as pH does not exceed 9. Surfactant concentration below 50 mg/dm^3 does not disturb the operation of the adapted sludge either; it only impedes the operation of aeration tanks. The biological treatment of textile WW pre-treated using the chemical precipitation method does not pose any difficulties.

Coagulation eliminates the basic load of dyes and dissolved substances from WW. Activated sludge easily adapts to the environment of these WW; however, the operation of a two-phase treatment plant is complex. The same final reduction rate of the pollution load and concentration is achieved for concentrated WW, or possibly total sewage, when preliminary fermentation is used. A technological system that uses anaerobic processes can also be recommended for many textile factories that deliver WW to the municipal sewage system, especially when local authorities object to the adverse influence of textile WW on the operation of the municipal sewage biological treatment plant.

It should be noted that textile WW (apart from flax industry WW) do not require any preliminary sedimentation. The amount of suspended solids after preliminary qualitative composition equalisation is always lower than 150 mg/dm^3. After two hours of sedimentation, sludge volume does not exceed 1 cm^3/dm^3, and the SS concentration reduction usually does not exceed 40%. Preliminary removal of SS from textile WW is thus not technologically justified.

Mechanism of Biological Removal of Impurities

WW may be treated biologically provided that polluting substances can be used as the nutritive substrate for micro-organisms. The adapted substrate is removed from the WW solution as a result of its transport in a water stream into cellular structures of micro-organisms through their surface. The micro-organisms' contact surface with the surrounding environment of WW treated is large. The unfolded surface of one gram of unicellular organisms and algae equals 1.1×10^{12} μm^2. For WW treatment with, for instance, activated sludge, the micro-organism mass concentration is about 3-6 kg/m^3, which corresponds to an unfolded contact surface of between 3300 and 6600 m^2/m^3.

It is the hydrolysis of polluting substances and the formation of enzyme-substrate structures, as well as the absence of toxic and inhibiting substances in the removed load of impurities, that allows the transport of polluting substances. The removal of impurities is a series process whose resultant velocity is determined by its slowest stage. The present author believes that the flow of the water stream containing adapted substrate structures is the slowest stage of this process. Actual biochemical reactions, so often emphasised in the literature on the subject, only take place in intracellular structures, and are the last stage of the process. The efficiency of biochemical reactions is then controlled by the velocity of the substrate transport to micro-organism cells in the water stream. A simple proof of this is the fact that a drop of water content in the environment surrounding micro-organisms below 40% causes a slowing-down and inhibition of the process [4].

According to biochemical criteria, the driving force of the process is the so-called homocellular system, which ensures the transport of nutrients to living cells (micro-reactors) even when the substrate concentration in the external environment is very low. It is believed then that the substrate flow occurs against the concentration gradient [5].

As a result of the occurrence of the phenomenon of the 'flow', the system 'sewage environment - micro-organism structures' should be treated as a defined vector velocity field that organises the travel of substrate-enzyme structures together with water particles. At the same time, the stream of water particles alone, as the smallest structures taking part in metabolism of living organisms, guarantees a zero water balance, i.e. the difference between the amount of the inflow, and the effluent in an area with the volume of the system examined (V) containing micro-organism structures with a mean concentration of X, is close to zero. The velocity field – i..e the vector field, regardless of the nature of determining factors (electric, magnetic, hydraulic) – characterises, in keeping with the general definition of the velocity field, the stream q induced by the velocity vector of particles that are in this field, $\bar{v}$. The characteristic stream of this field may be presented mathematically in the general formula

$$q = \iint_F \bar{v}\bar{n}\,dF \qquad (1)$$

For a defined mass of micro-organisms *X* that are in WW volume *V*, the velocity field may be considered to be homogenous, and the field stream may be expressed with the following formula:

$$q = KXV \qquad (2)$$

where:

q - the field stream, m^3/h

X - the micro-organism concentration in the system, kg/m^3

V - the volume of the system examined, m^3

K - the kinetic constant of the process, m^3/kgh.

The constant *K* is defined by the product:

$$K = v_n K'_p A_w$$

where:

v_n - the module of the projection of the vector of the velocity field stream $\bar{v}$ on the direction of the normal to the field surface, m/h

K'_p - the coefficient characterising the relationship between the total micro-organism contact surface and the active (exchange) surface

A_w - the mean specific surface of the micro-organisms, m^2/kg.

The total velocity field stream of a defined volume of treated WW, *V*, always fulfils the condition of zero water balance.

Tests for Biological Removal of Impurities

Biodegradation test

To examine the process of the loss of impurities, WW are usually tested using a preliminary biodegradation test. A drop in pollution concentrations is observed over defined time periods under the condition of lacking inflow of impurities from external sources. The periodic dynamics of the test may be presented in the following differential equation:

$$VdS = qS'dt - qSdt \qquad (3)$$

where (besides the determinations used in equations 1 and 2):

S - the substrate concentration (of removable impurities), kg/m^3

S' - the substrate concentration in the stream leaving micro-organism structures participating in the process, kg/m^3.

Using equation (2) and organising it with equation (3), the following relation is obtained:

$$-\frac{dS}{dt} = KX(S - S') \qquad (4)$$

In equation (4), it may be accepted that the product *KXS'* is proportional to the substrate concentration S_o at the beginning of the process:

$$KXS' = kS_o, \qquad (5)$$

then equation (4) is as follows:

$$-\frac{dS}{dt} = KX\left(S - \frac{kS_o}{KX}\right) \qquad (6)$$

possibly having determined:

$$\frac{k}{K} = k_1$$

$$-\frac{dS}{dt} = KX\left(S - k_1\frac{S_o}{X}\right) \qquad (7)$$

If the contact mass concentration *X* is constant in a given period, then after integrating equation (7), the following equation is obtained:

$$S = \frac{k_1 S_o}{X} + \left(\frac{S_o X - k_1 S_o}{X}\right)e^{-KXt} \qquad (8)$$

Determining in the formula above:

$$\frac{k_1 S_o}{X} = R_2;$$

$$\frac{S_o X - k_1 S_o}{X} = \bar{R}_2;$$

$$KX = K_o,$$

then the shortened notation of equation (8), describing the progress of the biodegradation process, is as follows:

$$S = R_2 + \bar{R}_2 e^{-K_o t} \qquad (9)$$

The nature of the substrate concentration changes described in the above equation is shown in Figure 1. The presented decrease in pollution concentration expressed by COD was determined to examine the

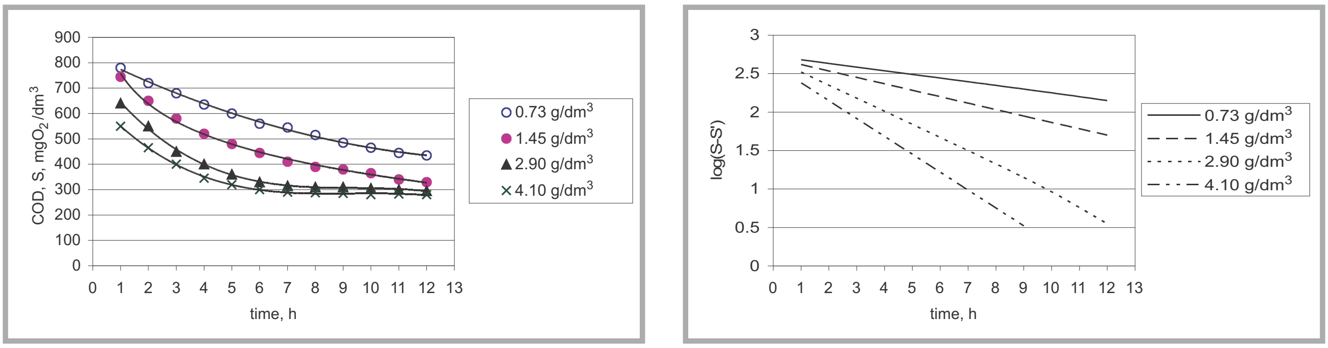

***Figure 1.** Decrease in pollution concentration (COD) in non-flow tanks for different micro-organism concentrations.*

process of biodegradation using activated sludge from a cotton industry plant [6]. As the analysis shows, pollution concentration in the recirculated stream (*S'*) was numerically close to the concentration of the unremovable substrate (*S'*=228 mg O$_2$/dm^3).

Thus, equation (9) may be rearranged into a linear form by finding its logarithm:

$$\lg(S - S') = \lg R_2 - 0.4343K_o t,$$

and then values K_o and K for different contact mass concentrations of activated sludge may be determined. The values of constant K_o were 0.1077; 0.2154; 0.4308; 0.6462 respectively; and of constant K, 0.1473; 0.1476; 0.1486; 0.1576 dm^3/gh.

Tests of continuous removal of impurities

When the substrate is continuously delivered to the contact chamber, which usually takes place in biological WW treatment, the fundamental mechanisms of the process, defined in statements (1-2), are retained.

The balance of the process which mostly occurs in complete mixing reactors is expressed by the following equation:

$$Q \cdot S_o - QS + qS' - qS = 0 \qquad (10)$$

where:

Q - the rate of sewage flowing to the reactor, m^3/h.

As on the basis of (2) $q=KXV$, then from equation (10)

$$S_o - S = KX\frac{V}{Q}S - KX\frac{V}{Q}S' \qquad (10a)$$

Determining above:

$S_o - S = S_R$ - removed pollution concentration

and

$\frac{V}{Q} = t$ - WW retention (aeration) time in the reactor,

then the following statement is obtained from (10a):

$$S = S' + \frac{1}{K} \cdot \frac{S_R}{Xt} \qquad (11)$$

and substituting: $S'=K'S_o$, and rearranging, the following equation is obtained:

$$\frac{S}{S_o} = K' + \frac{1}{K} \cdot \frac{\eta}{Xt} \qquad (12)$$

where:

η - treatment efficiency:

$$\eta = \frac{S_o - S}{S_o}.$$

The interpretation of continuous treatment in activated sludge reactors using the above equation makes it possible to achieve a very high degree of consistency in the results of experimental studies with the accepted model.

The findings for the cotton industry WW treatment in complete mixing chambers are given in Figure 2. Two laboratory aeration tanks were used in the studies conducted in the Department of Water Management at the Technical University of Łódź in 1999. WW retention times for each tank were 4 and 6 hours, and their active volume was 12 dm^3. Each tank was connected with a secondary settling tank whose volume was 3 dm^3. The pollution concentration in the inflow (S$_o$), determined as PV, ranged between 152 and 228 mg O$_2$/dm^3, while that of treated sewage (S) was between 64 and 88 mg O$_2$/dm^3.

Inflow concentration (expressed as COD) changed from S_o=480-888 mg O$_2$/dm^3, and was S=152-360 mg O$_2$/dm^3 after treatment. A distinct linear relationship consistent with equation (12) was obtained for the treatment results described by COD. The mean value of constant K for this indicator was 0.0465 dm^3/gh, and 0.298 dm^3/gh for oxygen demand. The values of constant K' also varied greatly for both indicators, and were 0.033 for COD and 0.285 for PV. A greater range of results was obtained for the retention time of 6 h, which may be explained by the fact that the mean sludge content in this tank ranged between 2.7 and 6.17 g/dm^3. In the tank with the retention time of 4 h, the amount of sludge was greater and at the same time steadier, ranging only between 5.58 and 6.74 g/dm^3. This influenced the indicator of sludge contact with WW for a defined aeration time (product $X \cdot t$), and thus the treatment outcome which was mostly influenced by the substrate (WW) quality change.

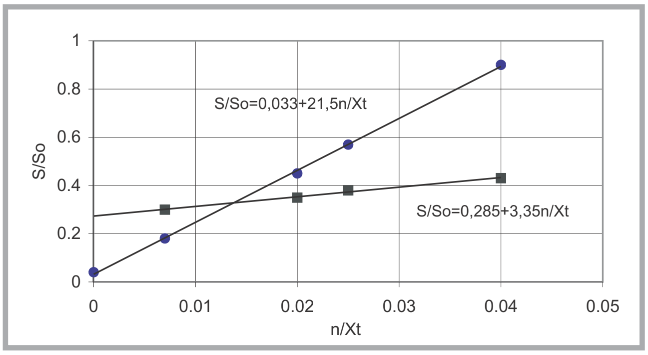

***Figure 2.** Textile WW treatment in complete mixing chambers with activated sludge (decrease in PV and COD); ● - COD + PV.*

Summary

Textile WW, having been technologically pre-processed in qualitative composition equalisation and neutralisation, may be treated biologically. In biological treatment, a load of impurities adapted by micro-organisms as a substrate is removed from WW. The substrate is used by micro-organisms for synthesis, regeneration and maintenance of living activity as a source of energy. The adapted impurities are part of the volatile substance load. Biological oxygen demand (BOD) is a measure for the adaptability of this pollution load by micro-organisms. Alternatively, other indicators characterising the presence of substances that oxidise easily, principally PV and COD, may be used, provided that BOD is also determined in the WW examined. If BOD is not detected in WW, then such WW are toxic.

Micro-organisms adapted to a specific nutritive substrate must be used in the biological treatment of textile WW, as only such groups tolerate toxic and inhibiting substances.

The loss of impurities from treated WW occurs as a result of the flow of available substrate structures into micro-organisms through the cell membrane in the water stream. Appropriate reactions and metabolic processes take place within micro-organisms that are miniature bio-reactors.

The values of standard pollution indicators of textile sewage, such as COD, BOD_5 and PV, fully confirm the consistence of the experiment results with the accepted interpretative model. At the same time, the parameters characteristic of the treatment processes in the non-flow system and the complete mixing system are also confirmed. Indicator equation (3) and balance equation (10) summarily present all the basic parameters necessary to describe biological treatment in conditions of the full adaptation of micro-organisms to the substrate.

For treatment of textile WW in which BOD is determined, the process of substrate removal in a biodegradation test is a continuous function over time.

Biological treatment is characterised by two parameters: concentration of unremovable substances S' and kinetic constant K_o proportional to the concentration of the micro-organism mass. The qualitative composition of micro-organisms determines the value of the constant K_o, which is the product of the constant K and the concentration of micro-organisms X, and which is influenced by the specific qualitative composition of the substrate. The constant K is a measure for the transport of the adapted substrate to the cells of micro-organisms, and may not be treated as a constant characteristic parameter, in the sense of the kinetics of chemical reactions. The constant K is exclusively a parameter of the kinetics of the process.

It should be noticed that in equation (9), which describes the change in the pollution concentration in non-flow tanks, the value R_2 may be determined approximately not only on the basis of the examinations but also analytically. The characteristic curve described by the equation shows that value R_2 may be determined from the relation:

$$R_2 = \frac{S_1 \cdot S_2 - S_3^2}{S_1 + S_2 - 2S_3}, \qquad (13)$$

where:

S_1, S_2 - any two extreme S values, read from the diagram of the treatment progress for any time t_1 and t_2, and

S_3 - corresponds to the value S read from the diagram for

$$t_3 = \frac{t_1 + t_2}{2}.$$

This condition is fulfilled by all the biodegradation curves obtained in the examinations in which the adapted mass of micro-organisms was used.

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