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## TREATMENT OF MIXED DYES AND MUNICIPAL WASTEWATERS BY ACTIVATED SLUDGE

For three years, the company Ekolog Systems has been engaged in establishment of a wastewater treatment plant in Zgierz. This plant operates under specific conditions because except a municipal wastewater line there is an important second line – wastewater containing the dyes from the “Boruta” Dyestuff Industry Works. The “Boruta” Dyestuff Industry Works is one of the biggest polluters in Poland. Our investigation was aimed at determining such proportions of mixed dye and municipal wastewater that allowed us to achieve a high efficiency of biological process. In the research programme, a mixture of municipal and dye manufacturing wastewaters was subjected to biological treatment. We observed that the contribution of dye wastewater could not be greater than 20% if we wanted to obtain high efficiency of treatment. When this contribution increased to 35% the amount of dry substance in activated sludge decreased from 3498 mg/dm<sup>3</sup> to 1471 mg/dm<sup>3</sup>. This situation arises because dyes are assigned to the compounds which are resistant to biodegradation.

### 1. INTRODUCTION

Ekolog System, Poznań, is involved in building a wastewater treatment plant in Zgierz. In order to test its treatability, a pilot plants was devised. In the pilot plant, mixed dyes and municipal wastewater are biologically treated. Dye wastewater is disposed of by “Boruta” Dyestuff Industry Works. “Boruta” produces mainly azo and sulphur dyes. The most important of them are azo dyes extensively used in textile and dyestuff industries. They have relatively complex structures and are resistant to microbial degradation [1]. Some of them are carcinogenic and mutagenic [2].

Generally, azo dyes contain azo linkages ( $-N=N-$ ) whose numer ranges from 1 to 3. They link phenyl and naphthyl radicals that usually occur in some combinations of functional groups including: amino ( $-NH_2-$ ); chloro ( $-Cl$ ), hydroxyl ( $-OH$ ), methyl ( $-CH_3$ ), nitro ( $-NO_2$ ) and sulfonic acid sodium salt ( $-SO_3Na$ ).

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Dyestuffs are practically nonbiodegradable during biological treatment, but they may be adsorbed by the sludge to the extent of about 40–80% or even more, depending on the individual dyestuff and treatment conditions. Investigations indicate that the extent of a dyestuff adsorption is determined by its structure, pH and composition of wastewater [3]. Composition of dye wastewaters is extremely variable due to the large number of dyes and other chemicals used in dyeing processes. Furthermore, dyes themselves are generally resistant to oxidative biodegradation, since one of the most important properties of commercial dyes is their resistance to fading caused by chemical- and light-induced oxidation [3]. Another problem with aerobic biological treatment of dye wastewater is the difficulty in acclimatizing the organism to the substrates.

## 2. MATERIAL AND METHODS

The thorough process in the pilot plant on a scale 1 to 10 000 which treats  $3.5 \text{ m}^3/\text{d}$  is approximated in the biological part to process train of the wastewater treatment plant in Zgierz. Wastewater was delivered to the pilot plant and, in future, to the wastewater treatment plant by two separate wastewater collection systems – municipal and industrial (dye wastewater from the “Boruta” Dyestuff Industry Works).

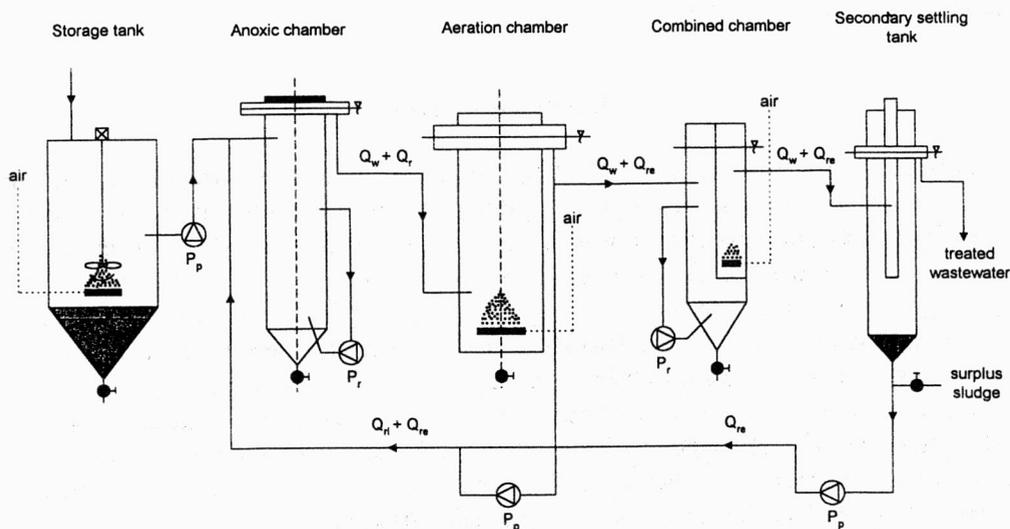


Fig. 1. Diagram of the pilot plant in Zgierz

$Q_{rw}$  – influent of the raw wastewater;  $Q_w$  – flow of the wastewater;  $Q_r$  – recirculated wastewater;  $Q_{re}$  – external recirculation;  $Q_{ri}$  – internal recirculation;  $P_r$  – rotodynamic pump;  $P_p$  – piston pump

Table 1

## Technical parameters of pilot plant

Parameters	Storage tank	Anoxic chamber	Aeration chamber	Combined tank	Secondary settling tank	Calibrating tank
General information	steel tank, cylinder-shaped with cone bottom	steel chamber, cylinder-shaped with cone bottom	steel chamber, cylinder-shaped with flat bottom	two-chamber steel tank, cylinder-shaped with cone bottom	steel tank cylinder-shaped with cone bottom	steel tank, rectangular-shaped, dimension 1.50×0.50×1.00 m
Diameter of the cylinder part [m]	1.60	0.60	1.20	0.80	0.60	1.50×0.50
Height of the cylinder [m]	2.00	3.40	–	2.60	3.40	–
Height of the cone [m]	1.25	0.40	–	0.60	0.40	–
Total height [m]	3.25	3.80	3.60	3.20	3.80	1.00
Total volume [m <sup>3</sup> ]	–	0.80	3.40	1.00	0.70	–
Hydraulic retention time [h]	–	5.50	23.20	6.80	4.80	–

The pilot plant was placed on the same site as wastewater treatment plant in Zgierz. The technological, gravitation system shown in schematic diagram (fig. 1) consists of the following tanks (compare table 1):

- storage tank,
- anoxic chamber,
- aeration chamber,
- combined tank (post anoxic, post aeration),
- settling tank,
- calibrating tank.

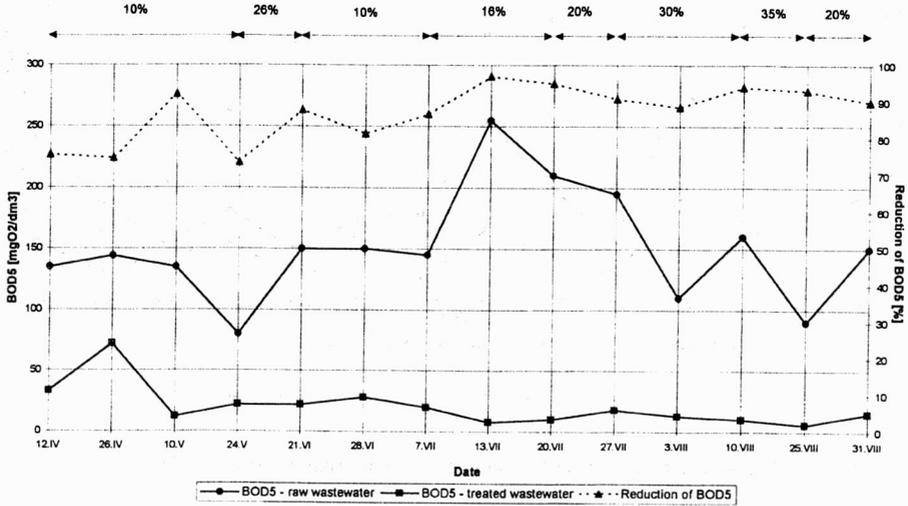
Two influent waste streams (municipal and dyestuff) were treated in separate primary treatment facilities. Common municipal and dye wastewaters were first subjected to preliminary treatment and then to biological treatment. Contrary to the full-scale plant, in the pilot plant operation the third step of the treatment (filters) and sludge handling are not applied. As mentioned above, preliminary treatment was carried out separately for municipal and dye wastewaters. Municipal wastewater was brought once a day by waste removal vehicle and stored without mixing in the storage tank. After a 1/2 hour, settled suspended solids were removed from the tank.

Dye wastewater from the industrial plant "Boruta" was preliminary neutralised, equalized and decanted outside of the pilot plant. The neutralized "Boruta" wastewater was then pumped once a day to the storage tank designed to store the municipal wastewater in the pilot plant. Air was sometimes stirred into wastewater in the tank to avoid sewage digestion and sedimentation of suspended solids. The combined wastewater was dosed, equally during the whole day, to the chamber where 4-Bardenpho process, i.e. a biological nutrient removal (BNR), took place. This 4-stage process allows biological nitrogen removal, while the 5-stage Bardenpho process enables the removal of both nitrogen and phosphorus. The 4-stage Bardenpho process proceeds if some chemicals facilitating phosphorus removal are added. In the first anoxic zone, nitrates in the internal recirculation ( $0.3 \text{ m}^3/\text{h}$ ) are used to oxidize influent organic compounds, producing nitrogen gas ( $\text{N}_2$ ) which is stripped from the wastewater. This process is known as denitrification. Biomass in the first aerobic phase converts the influent Total Kjeldahl Nitrogen (TKN) to nitrates (nitrification) and oxidizes influent organic compounds. A portion of the influent organic compounds is converted into new biomass. Additional denitrification takes place in the second anoxic zone. The mixed liquor is returned to this aerobic zone prior to secondary clarification (degree of external recirculation reaches  $0.15 \text{ m}^3/\text{h}$ ). In the secondary settling tank, which is located after the Bardenpho chamber, biological solids are separated from the clarifier effluent.

Samples were taken before anoxic chamber as raw mixed (municipal and dye) wastewater and after the secondary settling tank as treated wastewater. Starting up of the pilot plant began only with municipal wastewater. After a few days first 10% and then 16, 20, 26, 30, 35% of dye wastewater in comparison with the amount of whole wastewater began to be added.

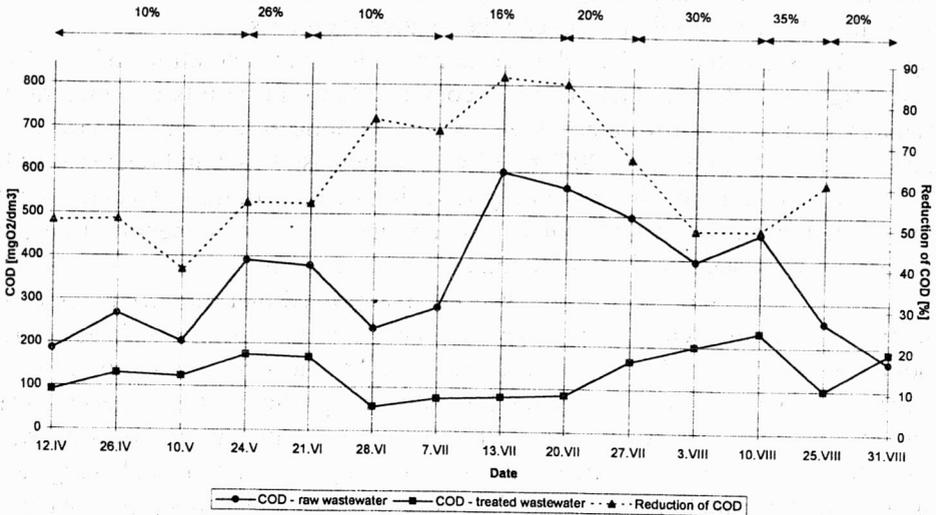
### 3. RESULTS AND DISCUSSION

As we mentioned, starting up of the pilot plant began when municipal wastewater was supplied. After a few days, about 10% of dye wastewater, compared to the



10, 16, 20, 26, 30, 35% - contribution of dyes wastewater in the amount of municipal wastewater

Fig. 2. Characteristics of wastewater – BOD<sub>5</sub>



10, 16, 20, 26, 30, 35% - contribution of dyes wastewater in the amount of municipal wastewater

Fig. 3. Characteristics of wastewater – COD

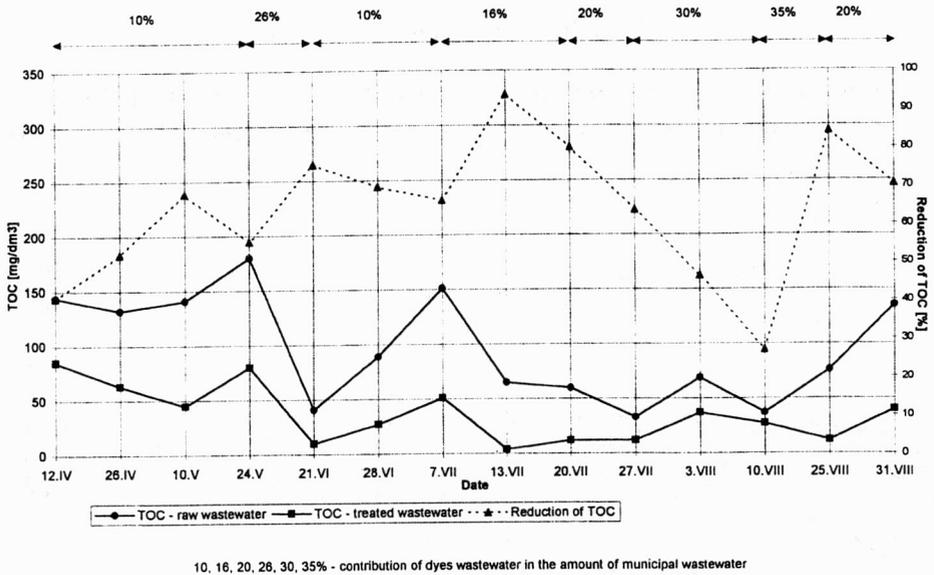


Fig. 4. Characteristics of wastewater – total organic carbon (TOC)

amount of whole wastewater, began to be added. At the beginning of mixing, perturbations in the work of activated sludge were observed. Activated sludge was more compact, the amount of filiform organisms decreased, but the amount of ciliate organisms increased. In the supernatant liquid, there were particles whose sedimentation was difficult, which adversely influenced the treatment process.

Figures 2–8 show the results achieved during pilot plant operation. BOD<sub>5</sub>, COD and TOC (figures 2, 3, 4) reductions were comparable to the results obtained during treatment of municipal wastewater. However, it was noticed that the increase in the amount of dye wastewater from 20% to 35% may increase COD and decrease BOD<sub>5</sub> in the effluent. Such a situation is indicative of high concentration of nearly nondegradable compounds. The COD/BOD<sub>5</sub> ratio confirms this phenomenon (figure 5). Figure 6 shows the concentration of the total suspended solids.

The first two analyses (10% of dye wastewater) proved that the efficiency of the nitrification and denitrification processes gradually increased (figures 7, 8). During one month, the reduction of nitrogen reached 99%. At that time, minimum growth of the activated sludge was observed although surplus sludge did not leave the secondary settling tank. After a few days, we decided to increase the amount of dye wastewater from 10% to 26%. A slight tendency to decrease the capacity of activated sludge after 15 minutes of sedimentation was noticed (table 2). At the same time, the concentration of the activated sludge decreased from 1200 mg/dm<sup>3</sup> to 940 mg/dm<sup>3</sup> (figure 9). Also the sludge volume after 15 minutes of sedimentation decreased from 100 to

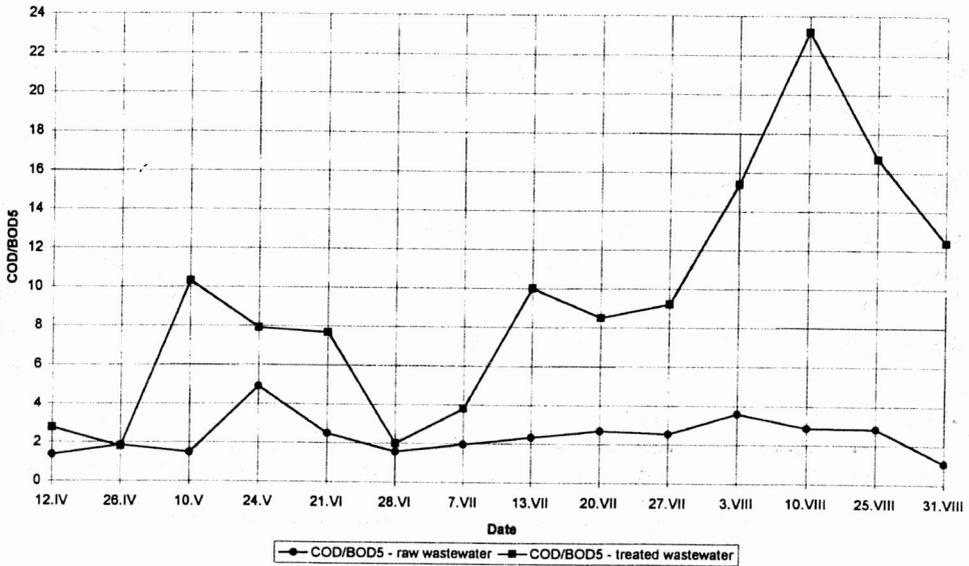
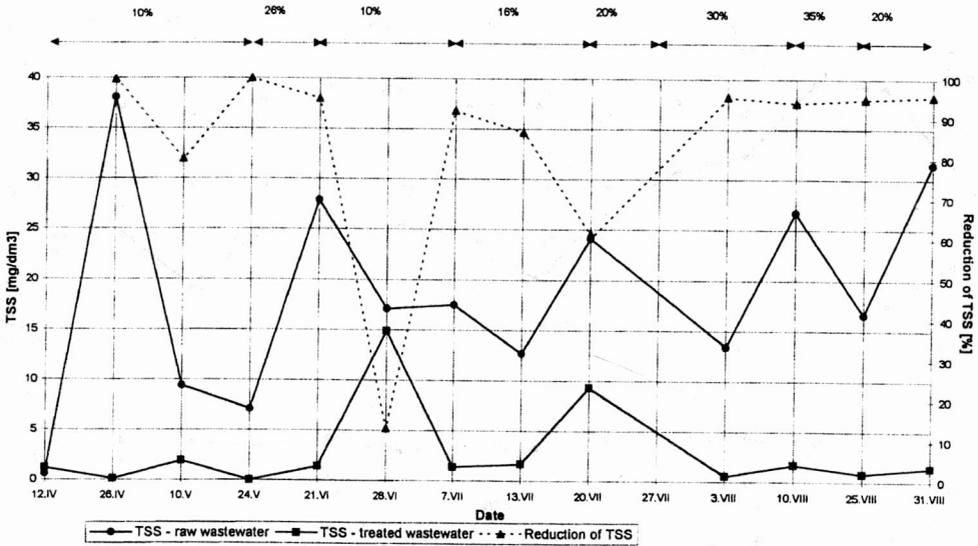


Fig. 5. Characteristics of wastewater – COD/BOD<sub>5</sub>



10, 16, 20, 26, 30, 35% - contribution of dyes wastewater in the amount of municipal wastewater

Fig. 6. Characteristics of wastewater – total suspended solids (TSS)

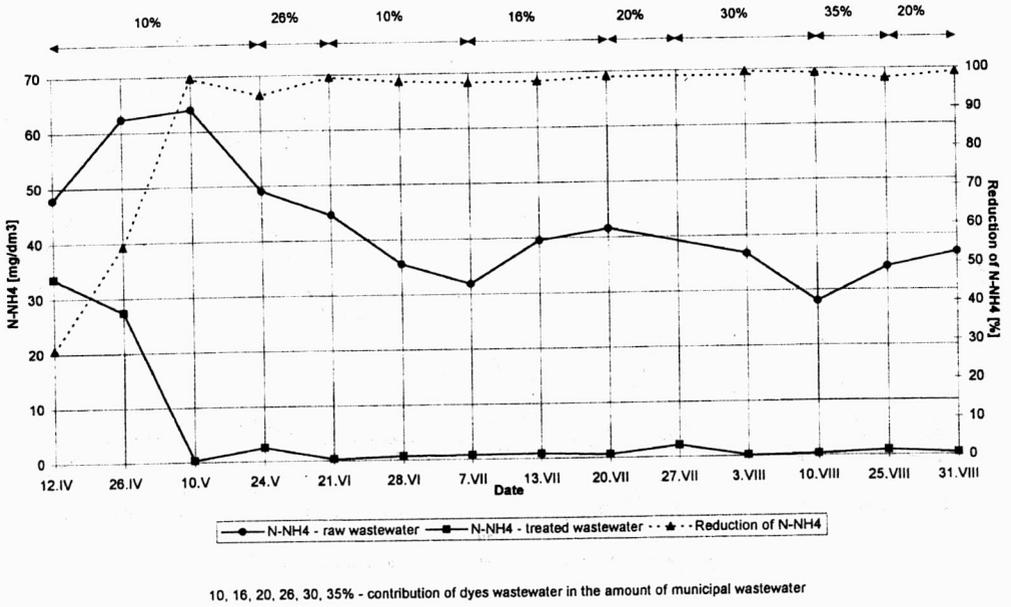


Fig. 7. Characteristics of wastewater - N-NH<sub>4</sub>

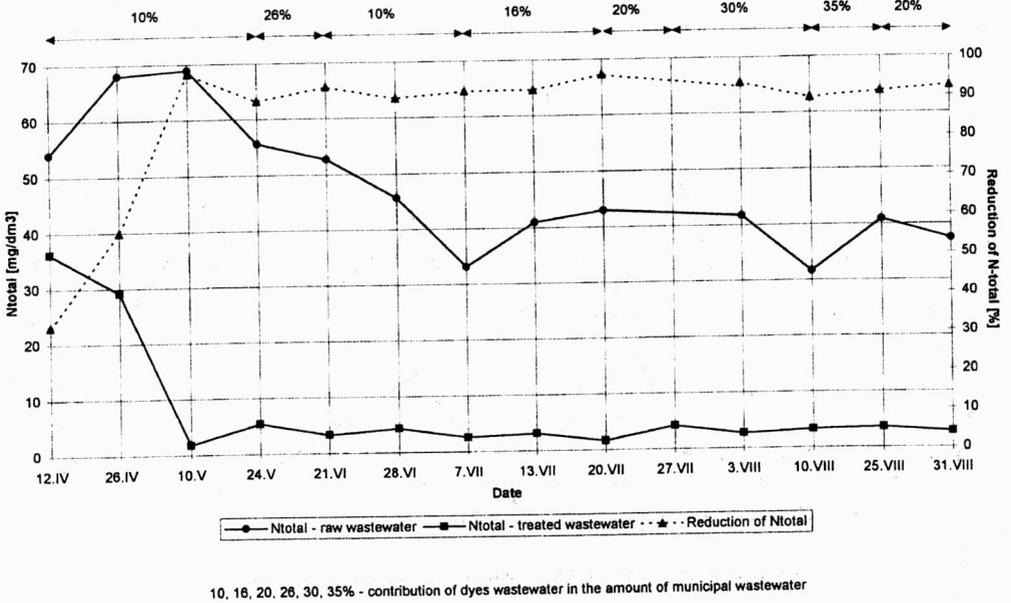


Fig. 8. Characteristics of wastewater - total N

Table 2

## Characteristics of activated sludge

Date	Contribution of dye wastewater in the volume of whole wastewater [%]	Contents of mixed liquid suspended solids [mg/dm <sup>3</sup> ]	Capacity of activated sludge after 15 min of sedimentation [cm <sup>3</sup> /500 cm <sup>3</sup> ]	BOD [mg O <sub>2</sub> /dm <sup>3</sup> ]	COD [mg O <sub>2</sub> /dm <sup>3</sup> ]	Sludge loading [kg BOD/(kg dry solids×d)]	Sludge loading [kg COD/(kg dry solids×d)]	Sludge volume index [cm <sup>3</sup> /g]
12.04	≈ 10	972	65	135	186	0.09	0.12	82.3
26.04	≈ 10	1100	70	144	268	0.08	0.16	91.0
10.05	≈ 10	1219.6	100	135	204	0.07	0.11	114.8
24.05	≈ 26	939	55	80	392	0.05	0.27	106.5
21.06	≈ 10	2185	75	150	380	0.04	0.11	59.5
28.06	≈ 10	1778	65	150	236	0.05	0.08	50.3
07.07	≈ 16	2088	62	145	286	0.04	0.09	50.3
13.07	≈ 16	3498	100	255	600	0.05	0.11	60.0
20.07	≈ 20	3280	100	210	564	0.04	0.11	61.0
27.07	≈ 30	3094	87	195	498	0.04	0.10	56.2
03.08	≈ 30	2452	82	110	396	0.03	0.10	66.9
10.08	≈ 35	1471	75	160	460	0.07	0.20	81.5
25.08	≈ 30	2286	75	90	256	0.03	0.07	60.0
31.08	≈ 30	2004	75	150	164	0.05	0.05	56.9

Treatment of mixed dyes

50 cm<sup>3</sup>/500 cm<sup>3</sup>. In this case, we decided upon the rebuilding of activated sludge by the elimination of dye wastewater for a few days. After three weeks the concentration of activated sludge increased to about 2000 mg/dm<sup>3</sup>, although its volume after 15 minutes of sedimentation was not higher than 80 cm<sup>3</sup>/500 cm<sup>3</sup>. This period was characterised by large amount of suspended solids ( $\approx 100$  mg/dm<sup>3</sup>) and intensive colouring caused by dye wastewater. In order to know the contribution of a particular pollutant index before mixing, we decided to extend the range of analysis of municipal raw wastewater and dye raw wastewater from July. Although the activated sludge stabilised, we introduced a new portion of it to obtain the concentration of activated sludge of about 3000–4000 mg/dm<sup>3</sup> consistent with design (figure 9). The concentration of

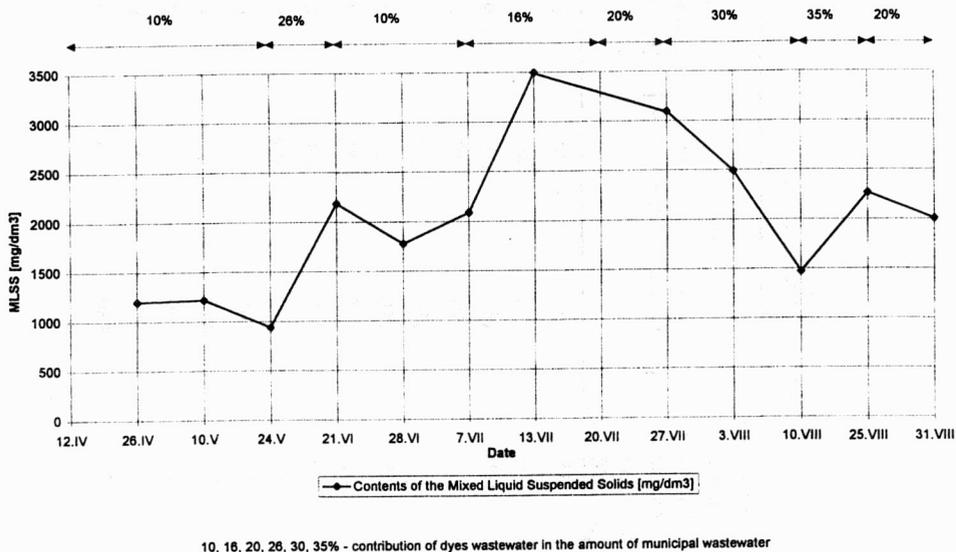


Fig. 9. Characteristics of wastewater – mixed liquid suspended solids (MLSS)

activated sludge increased from 2088 mg/dm<sup>3</sup> to 3498 mg/dm<sup>3</sup>. At this moment, the contribution of dye wastewater increased from 16% to 20, 30% and by the end achieved 35% of the whole volume. During that time, the concentration of activated sludge decreased from 3498 mg/dm<sup>3</sup> to 1471 mg/dm<sup>3</sup> (at the end of the work with 35% contribution of dye wastewater). We did not deal once again with the situation from a few weeks ago, thus we decided to decrease the percentage participation of dye wastewater from “Boruta” to ca. 20%. After decreasing the contribution of dye wastewater, the concentration of activated sludge increased for over two week from 1471 mg/dm<sup>3</sup> to 2286 mg/dm<sup>3</sup>. At this moment, we decided to increase the contribution of dye wastewater to 30%. High efficiency of wastewater treatment is attained if the contribution of dye wastewater is not higher than 20%.

#### 4. CONCLUSIONS

1. In order to treat mixed dyes and municipal wastewater by the activated sludge method, we have to adopt gradually the sludge to the treatment environment which allows its work under inconvenient conditions and high efficiency of the treatment. Activated sludge adapted to unfavourable conditions is more compact compared to the typical, which can be confirmed by low value of SVI (sludge volume index).

2. High treatment efficiency of adapted activated sludge can be sustained when the contribution of dye wastewater does not exceed ca. 20% of the whole wastewater inflow to the biological reactors. The higher contribution can cause gradual decay and dispersion of activated sludge. The proportions mentioned above refer to municipal wastewater after preliminary treatment and to dye wastewater after neutralisation and mechanical treating.

3. Decay and dispersion of activated sludge due to higher doses of dye wastewater never take place immediately during investigations. This process always goes on for a long time which gives time to counteraction.

4. In biological process, really high efficiency of the nitrogen removal was observed. With a relatively weak growth of the surplus sludge (unusual environment for the activated sludge) it was noticeable that the nitrogen removal took place mainly during denitrification process. It was proved by large amounts of gaseous nitrogen released in the denitrification chambers and low concentration of total nitrogen in the effluent.

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#### OCZYSZCZANIE ZMIESZANYCH ŚCIEKÓW BARWIARSKICH I MIEJSKICH METODĄ OSADU CZYNNEGO

Firma Ekolog Systems przez ponad trzy lata była zaangażowana w budowę oczyszczalni ścieków w Zgierzu. Oczyszczalnia ta jest specyficzna, gdyż oczyszcza się w niej zmieszane ścieki miejskie i barwiarskie. Ścieki barwiarskie pochodziły z Zakładu Produkcji Barwników „Boruta”, który znajduje się na liście przedsiębiorstw najbardziej zanieczyszczających środowisko.

Przedstawione badania pozwoliły określić dopuszczalny procent ścieków barwiarskich w ich mieszaninie ze ściekami miejskimi, umożliwiającą uzyskanie wymaganych efektów oczyszczania. Zaobserwowano, że maksymalny udział ścieków barwiarskich w mieszaninie ścieków nie może przekraczać 20%. Zwiększenie udziału ścieków barwiarskich do 35% powodowało zmniejszenie stężenia osadu czynnego z  $3498 \text{ mg/dm}^3$  do  $1471 \text{ mg/dm}^3$ .