Treatment efficiency of dyed wastewater

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Introduction

Protection of surface water is one of the most important tasks of modern environmental protection. It can be realized by reducing discharges of untreated industrial wastewater to the receivers, a comprehensive treatment of the wastewater and the closing water circuits in manufacturing plants.

Rapid changes in production and application technology, as well as a variety of types dyes currently used in various industries (since the discovery of the first synthetic dye 150 years ago, approx. 10 000 various dyes were put into production [1]) make it difficult to develop a simple, universal, and furthermore effective and economical methods for removing dyes from wastewater.

The variety of steps and technologies used in the processing and finishing of fabrics does not allow to define the typical production process. For this reason also a typical composition and typical volume of generated wastewater cannot be specified. The processes in textile plants, such as washing, bleaching, softening, coloring, etc., generate a variety of contaminants in the process waters like fats, waxes, bleaches, dextrin, dyes and detergents. The wastewater after the dyeing process also contains a substantial amount of salt (NaCl or Na_2SO_4) and organic and inorganic chemical additives (acids or alkalis, leveling agents, thickeners, sodium hydrosulfite, detergents, ammonium sulfate and ammonium acetate, oxidizing agents, etc.). Their concentration in the wastewater is close to the initial concentration because they are not consumed. Their task is to create the appropriate conditions for the proper conduct of the dyeing process. The composition and amount of generated wastewater depends on the type of colored material (cotton, wool, synthetic fibers) and its form (fiber, yarn, a tow windings, textile, finished goods), dye method (periodic, continuous or semi-continuous), the intensity of staining [2]. The basic pollution load comes from bleaching and dyeing.

Textile industry is widely regarded as consuming large quantities of water. The volume of water generated in the plants involved in the processing and finishing of fabrics (including coloring and modifications to impart specific properties) may reach values of 100 dm^3/kg of raw material for products of synthetic fibers, up to more than 300 dm^3/kg for wool textiles [3], and it is equal to approx. 90% of the amount of water consumed. The remaining 10% is evaporated, or is lifted with the fiber [2].

Treatment of textile wastewater can be done in three ways: in biological wastewater treatment plant on the premises, in the municipal wastewater treatment plant off site, by selection of separate wastewater streams and treatment inside or outside the facility. The effectiveness of biological treatment depends primarily on the averaging of sewage and on offset their flow into the tanks of activated sludge. The best purification results are achieved by mixing dyed wastewater with domestic wastewater in a ratio of 1:1. Removal of color from the wastewater may, however, be the result of adsorption on the microbial cells of activated sludge than of their biodegradability [4]. Another aspect of the biological treatment is bacteriostatic effect of some dyes, which may interfere with the proper operation of the activated sludge [5].

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Together with biological wastewater treatment methods, mechanical purification is commonly used. During the two-hour sedimentation 40–50% reduction of suspensions, 15–20% reduction of color and reduction of BOD_5 values from 8 to 40% can be obtained [2].

A filtration, centrifugation, coagulation with calcium or aluminum salts may also be used for the textile wastewater treatment. The most popular chemical methods are neutralization and oxidation (with chlorine compounds or ozone) [6]. Among the physicochemical methods of textile wastewater treatment coagulation, electrocoagulation, flocculation, co-precipitation, electrolysis, flotation and sorption are used. One of the most used membrane methods is the ultrafiltration. Reverse osmosis enables the water recovery and the resulting concentrate can be used repeatedly in the dyeing process.

Despite the many available methods of effective treatment of textile industrial wastewater, in Polish manufacturing plants the purification process is often limited to holding wastewater in the sedimentation tanks. Sometimes selected wastewater streams are chemically pretreated, mixed with wastewater from other departments and then discharged into the municipal sewerage system or to the receiver.

The direction of changes in the textile industry should take into account both the economic (the competitiveness of individual plants on the market), as well as ecological aspects. According to the assumptions of sustainable development, the modern plants involved in the processing and finishing of textiles, should primarily seek to limit water and energy consumption (eg. by returning a part of processing water), to limit the use of chemicals, dyes and additives, reducing the amount of generated wastewater and emissions of pollutants into the waters and the atmosphere.

The study presents an analysis of the actual effectiveness of treatment of wastewater from dyeing plants, on the example of five dyeing works located in the Lodz region. As part of the work a series of checkups of the actual values of the wastewater parameters before and after treatment in selected facilities was carried out, before discharge of wastewater into the municipal sewage system (in accordance with the Resolution of the City Council in Lodz No. XIX/239/03 of 24.09.2003r. on the introduction of the "Regulations of providing water and sewage disposal in the city of Lodz").

Materials and methods

The wastewater for study was taken from 5 dying works located in the Lodz region. From each of works two samples were collected, the raw one and the second one after treatment in wastewater treatment on the premises. In the collected effluents determinations of COD by the dichromate method, content of chlorides (by the argentometric method), the level of pH, the content of suspensions, dry residue and the solutes (by weighing method) was determined. The spectrophotometric analysis of tested samples was also carried out.

Characteristics of dyeing works

Works 1

The works deals with dyeing of jacquard and flat knitted and woven, made of the following materials: cotton, polyester, viscose, wool, spandex and polyurethane. The coloring agents used are reactive, disperse, direct and acid dyes.

The amount of sewage discharged into the municipal sewage system is about 30 m^3/h. Dyeing works is equipped with mechanical wastewater treatment plant on the premises using processes – filtration, sedimentation and neutralization and recovery of thermal energy. Ultimately, the plant intends to expand the sewage treatment system with membrane technology.

Works II

Second dye works deals with the dyeing of fabrics such as cotton, viscose, polyester, polyamide, wool, acrylic. Applied groups of dyes are reactive, disperse and acid dyes.

The dyeing works has its own wastewater treatment plant which uses transitional tanks in which the temperature is averaged by heat recovery and the parameter pH – with hydrochloric acid.

Works III

It handles dyeing of a wide range of textile products. The dyes used in the dye works: acid and metal complex, reactive bifunctional concentrated, reactive multifunctional, disperse. The facility uses an open horizontal flow sedimentation tank to wastewater treatment. The amount of wastewater generated is about 50 m^3/h. Of the three clarifiers two are closed, together with the aerator. Wastewater goes by the closed canal to the clarifier, which leads directly into the municipal sewage system.

Works IV

In the way of wastewater treatment this plant is the most advanced dye works among all described. It specializes in dyeing, bleaching, washing, refining, finishing and digital printing of knitted and woven cotton, viscose, polyester, polyamide, wool, acrylic and others.

Wastewater from dye works are divided into two groups: susceptible to biological treatment and the hard biodegradable, which is treated by chemical methods. Dye works discharged approx. 75m^3 of wastewater per hour.

Sewage treatment plant located on the premises comprises a plurality of modules for wastewater pretreatment: expansion tank, drum screen filter for separation of solid particles, tubular heat exchanger, adjustment of the pH and coagulation (module uses an innovative method of biocoagulation by selection of a biodegradable coagulant), three step bioreactor system, ozonation, sludge stabilization.

Works V

Works V is the smallest of the facilities discussed. Its production is based on dyeing fabrics such as lycra, microfiber and stretch using metal complex and acid dyes.

Table 1

The physicochemical parameters of wastewater from selected dye works engaged in dyeing and finishing of textiles (data obtained from plants) and the limit values specified in the Resolution of the City Council in Lodz of 24th September 2003

Pollution indicators	Unit	Average values					Limit values
		I	II	III	IV	V	
Temperature	°C	29.8–31.5	29.8–31.5	18–22	18–22	37–40	< 35
pH	-	7.93–9.47	7.7–8.3	6.9–7.2	6.5–8.0	5.4–5.2	6.5–9.5
BOD_5	mgO_2/dm^3	310	57	152	202	450	500
COD_{Cr}	mgO_2/dm^3	692	230	355	405	956	1000
Chlorides	$mgCl^-/dm^3$	322	1284	311	382	189	2000
Ammonia nitrogen	mg $N\text{-}NH_4/dm^3$	20.3	0.73	4.2	5.5	17	30
Anionic surfactants	mg/dm^3	2.15	0.54	6.7	5.7	11	15
Total phosphorus	mg P/dm^3	4.45	4.45	2.5	4.1	6.2	15
Sulphate	mg $/dm^3$	24.2	80	187	192	202	500
Suspended solids	mg/dm^3	268	129	87	120	320	450
Ester extract	mg/dm^3	21.8	19.9	25	32	42	100

The effluent from the dyeing process are mechanically pre-treated on screens. During the second stage it goes to a clarifier where a coagulation process with aluminum sulfate take place.

Table 1 summarizes the quality of wastewater discharge (according to data provided by the individual facilities) and compares them with the Resolution of the City Council in Lodz No. XIX/239/03 of 24.09.2003r. on the introduction of the "Regulations of providing water and sewage in the city of Lodz".

Spectrophotometric analysis of tested samples

For the spectrophotometric study of sewage samples the spectrophotometer HITACHI U-2800 and dedicated software of UV HITACHI SOLUTIONS were used. Spectra graphs were plotted in the wavelength range from 340 to 800 nm. Spectra of samples: raw, purified, raw after centrifugation and purified after centrifugation were made. In order to determine the degree of reduction in color after wastewater treatment, area under the graph for each spectrum was estimated by the numerical method of approximate calculating definite integrals.

Results and discussion

Spectrophotometric analysis

Spectrophotometric analysis showed that the most commonly used coloring agents in plants are violet-blue dyes. The degree of removal of color from raw wastewater and wastewater subjected to a purification process of the selected plants is vary widely. Due to the lack of adequate regulation in legislation, treatment of wastewater in sewage treatment plant in dye works does not provide for the removal of color.

Figure 1 shows an example of the spectrum of sewage samples collected in Facility III. The graph shows both samples of raw wastewater, and after the treatment process. Due to the high turbidity, samples of both types of wastewater was centrifuged and their spectra were also analyzed. The same procedure was used for sewage samples taken from other dyeing plants in Lodz and the surrounding area.

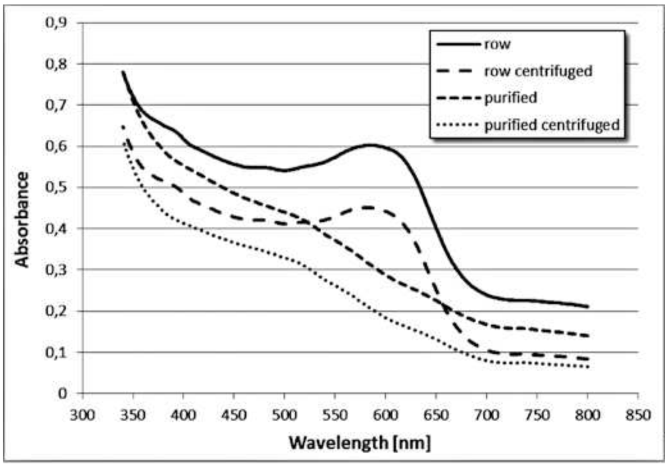

Fig. 1. Example of a spectrophotometric analysis of raw and purified wastewater. Samples were taken from the Works III

Table 2 shows the results of spectral analysis of the wastewater samples. Due to the presence of several coloring agents, the degree of color and suspension reduction in the examined wastewater were determined based on the differences in the surface areas under the curves of the spectra.

The decrease in absorbance of the solutions may occur as a result of discoloration or diminution of the amount of suspensions that effectively reduce the light permeability. In the samples analyzed only centrifugation of raw wastewater reduced the absorbance from

6 to 53% (Facility II). The analyzes also indicate that high volume of suspensions remains in the wastewater after treatment (in two cases centrifugation these samples resulted in a further decrease in absorbance by 20% relative to the raw wastewater).

Table 2

The degree of reduction (%) of color and the turbidity in the treated sewage in relation to the raw wastewater

Works	Row centrifuged	Purified	Purified centri-fuged
Works I	6.32	41.09	47.02
Works II	52.77	45.54	65.38
Works III	24.67	18.51	39.75
Works IV	22.75	69.70	73.17
Works V	11.02	-19.57	-0.31

Table 3 shows the results of chemical analysis of wastewater samples taken from dyeing plants. The results concern raw samples (taken after the completion of the dyeing process) and treated wastewater, discharged into the municipal sewage system. The percentage changes of selected parameters in treated wastewater with respect to the raw wastewater was also determined. These parameters which exceed the limits specified in the Resolution of the City Council in Lodz are marked.

Table 3

Summary of the parameters analyzed in the tested raw wastewater and after the treatment process from dyeing plants selected in the Lodz region (values exceeding the standards contained in the Resolution are indicated in bold)

Works	Sample	pH	COD [mgO$_2$/dm^3] % red	Chloride [mg/dm^3] % red.	TSS [mg/dm^3] % red.	Dry residue [mg/dm^3] % red.	Solutes [mg/dm^3] % red.
I	Row	7.56	915	1420	37	3188	3151
	Purified	7.78	455 50%	710 50%	40 -8%	1360 57%	1320 58%
II	Row	9.27	928	130	113	1135	1022
	Purified	7.14	1055 – 14%	1331 – 924%	86 24%	3312 – 192%	3226 – 216%
III	Row	10.04	1344	976	54	2016	1962
	Purified	**10.11**	799 41%	1420 – 45%	80 -48%	1603 20%	1523 22%
IV	Row	9.30	1874	350	44	4554	4510
	Purified	8.62	786 58%	335 4%	2 95%	3135 31%	3133 31%
V	Row	4.80	1028	290	27	1132	1105
	Purified	**4.35**	**2520** -145%	415 - 43%	**1119** - 4044%	1682 - 49%	563 49%

The results of the analysis of chemical oxygen demand indicates that in two cases out of five (Works II and V) treatment of wastewater in sewage treatment plants on-site do not meet the requirements enabling them to discharge to the municipal sewage system. Exceeding standards for COD is probably due to high content of organic compounds due to the poor technical condition of clarifiers.

In the presented analysis in one case (Works II) the permissible amount of the suspension exceeds the statutory standards. This is due to improper maintenance of clarifier (too much humic compounds and fat).

The dry residue, which is the sum of the suspensions and solutes in two cases out of five was not reduced. The amount of solutes depends mainly on the amount of additives used in the dyeing process such as salt, glauber salt, ammoniac soda, caustic soda, acetic acid, hydrogen peroxide, hydrosulfite, or ammonium sulphate. In one case out of five, the amount of solutes significantly increased after the purification process. This increase is correlated with a significant increase in the amount of chloride in the examined sewage. During the process Works II uses hydrochloric acid to neutralize relatively high alkalinity, which may cause increased levels of both chlorides and total solutes.

Conclusions

Despite the collapse of the textile industry in the Lodz region, still in Lodz and in the surrounding area there are many manufacturing plants involved in dyeing and finishing fabrics. The wastewater produced in these works are mainly characterized by a strong color, variable amounts of various kinds of chemicals and acidic or alkaline pH.

The wastewater from all analyzed dyeing works is discharged into municipal sewers. Therefore their parameters does not have to meet strict standards for wastewater discharged directly into waters or into the ground [7]. In addition, Group Wastewater Treatment Plant in Lodz, receiving sewage from analyzed dyeing works, is calculated per 1 million population equivalents, and the average size of sewage inflow reaches 195.6 thousands m^3/day. So, it is not sensitive to even very irregular discharges of highly polluted wastewater. Nevertheless, concern for the environment and local regulations defining limit values of effluents discharged into the municipal sewage system, require the use of technology of colored wastewater pretreatment from plants located in Lodz and its surroundings. Due to the poor technical condition of devices used to eliminate the contaminants from the process waters (clarifier), in the Facility V exceedance of the permissible values of wastewater was observed, despite correct values declared by works. Overgrown and polluted clarifier (which is also receiver of domestic sewage of the plant) is an additional source of humic compounds and fats in wastewater discharged into drains.

Only one of the analyzed dyeing works (Facility IV) has a developed, multi-modular wastewater treatment system, with recycling of part of process water and the recovery of heat and part of the chemicals [8]. The project of wastewater treatment and closing of water circuits is carried out under the guidelines of BAT – Best Available Technics for the textile industry [9]. As a result, approx. 58% decrease in the value of COD, 95% reduction in total suspended solids and a 70% reduction in color are obtained. This company is one of the most modern dye works in Poland. It often introduces and tests innovative solutions both in the field of dyeing and wastewater treatment processes.

In most of the analyzed cases wastewater from dyeing plants in Lodz and the surrounding area meet the legal standards. However, these standards do not currently include all the parameters that may affect the microorganisms of activated sludge or biofilm beds such as heavy metals content (coming from the metal complex dyes) or toxicity of wastewater. In large wastewater treatment plants, as in Lodz, industrial sewage are diluted significantly by municipal wastewater and urban run-off. In the case of small biological treatment plants, discharge of wastewater from dye works may interfere with their function.

Literature

1. Czajkowski W.: Nowoczesne barwniki dla włókiennictwa: Wydawnictwo Politechniki Łódzkiej; 2006, str.5.

2. Anielak A. M.: Chemiczne i fizykochemiczne oczyszczanie ścieków. PWN, 2002, str. 291–306.
3. Mihułka M.: Charakterystyka technologiczna przemysłu włókienniczego w Unii Europejskiej. Ministerstwo Środowiska, 2003.
4. Kapdan I. K., Kargi F.: Simultaneous biodegradation and adsorption of textile dyestuff in an activated sludge unit. Process Biochemistry. 2002, **37(9)**, 973–81.
5. Shahmoradi Ghaheh F., Mortazavi S. M., Alihosseini F., Fassihi A., Shams Nateri A., Abedi D.: Assessment of antibacterial activity of wool fabrics dyed with natural dyes. Journal of Cleaner Production. 2014, **72**, 139–45.
6. Constapel M., Schellentrager M., Marzinkowski J., Gab S.: Degradation of reactive dyes in wastewater from the textile industry by ozone: Analysis of the products by accurate masses. Water Research. 2009, **43(3)**, 733–43.
7. Dz.U 2006 nr137, Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006 r.w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego.
8. Bilińska L., Bemska J., Biliński K., Ledakowicz S.: Zintegrowana chemiczno-biologiczna oczyszczalnia ścieków włókienniczych. Inżynieria i Aparatura Chemiczna. 2012, **51(4)**, 95–97.
9. European Commission, 2003. Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Technics for the Textiles Industry.

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Aktualności z firm

News from the Companies

Dokończenie ze strony 153

Laboratorium Kariery Polpharmy – ruszyła I edycja programu stażowego

18 wybitnie uzdolnionych absolwentów i studentów rozpoczęło roczne staże w Oddziale Biotechnologii Polpharmy w ramach I edycji programu Laboratorium Kariery. Uczestnicy I edycji Laboratorium Kariery, to absolwenci i studenci takich kierunków studiów, jak biotechnologia, biologia, chemia i farmacja. Przez rok będą współpracować z zespołem Oddziału Biotechnologii Polpharmy w Gdańskim Parku Naukowo-Technologicznym. Program umożliwia zdobycie doświadczenia oraz dalszy rozwój dzięki pracy w najnowocześniejszym ośrodku biotechnologicznym w Polsce. Laboratorium Kariery jest programem Polpharmy oferującym specjalistyczne staże w wybranych obszarach biznesowych Grupy. Projekt został stworzony z myślą o młodych i ambitnych osobach, które dopiero zaczynają budować swoją ścieżkę kariery i daje możliwość rozwoju osobistego dzięki inspirującym warsztatom szkoleniowym i profilowanej ścieżce rozwoju kariery. *(kk)*

(http://www.polpharma.pl/, 11.03.2016)

„Szybka ścieżka" – dla mikro, małych i średnich przedsiębiorstw ponownie otwarta

Narodowe Centrum Badań i Rozwoju ogłosiło konkurs tzw. szybkiej ścieżki dla MŚP. Na wsparcie innowacyjnych projektów polskich przedsiębiorców przeznaczy 750 mln PLN. To trzeci konkurs NCBR w ramach poddziałania 1.1.1 „Badania przemysłowe i prace rozwojowe realizowane przez przedsiębiorstwa" PO IR, którego celem jest podniesienie innowacyjności polskich przedsiębiorstw poprzez wykorzystywanie rezultatów prac B+R w prowadzonej działalności gospodarczej. Jego nowatorska formuła – ograniczenie formalności do niezbędnego minimum oraz krótki czas wydania decyzji – jest bardzo atrakcyjna dla firm. Jednocześnie ambitne kryteria konkursu zapewniają, że wsparcie ze środków publicznych otrzymają przedsiębiorstwa realizujące ambitne projekty, które przełożą się na wzrost innowacyjności polskiej gospodarki. Nabór wniosków będzie prowadzony od 4 kwietnia do 29 lipca 2016 r., a co miesiąc NCBR będzie zamykał turę naboru, by w ciągu ok. 60 dni przedsiębiorcy, którzy aplikowali w danej turze otrzymali decyzję w sprawie dofinansowania. *(kk)*

(http://www.ncbir.pl/, 1.03.2016)

SPOTKANIA

Bezpieczne Praktyki i Środowisko

1 marca br. Komisja Młodzieży FSNT-NOT podsumowała w Warszawie Program „Bezpieczne Praktyki i Środowisko" za 2015 r. oraz zainaugurowała trzynastą edycję Programu na 2016 r. W posiedzeniu wzięli udział główni partnerzy Programu, Partnerzy Honorowi, sygnatariusze Listu Intencyjnego, przedstawiciele ZG FSNT-NOT, inicjator programu Roman Długi, przewodniczący Komisji Młodzieży Artur Badyda, Zarząd Forum Uczelni Technicznych, reprezentanci samorządów studenckich uczelni technicznych oraz organizatorzy regionalni Programu.

Głównym celem projektu jest zapoznanie młodych ludzi podejmujących staż, praktykę lub po raz pierwszy pracę zawodową, z prawami i obowiązkami pracowniczymi oraz z zagrożeniami dla zdrowia i bezpieczeństwa w czasie pracy; z przepisami Kodeksu Pracy i innych regulacji prawnych, w tym zwłaszcza z zasadami bezpieczeństwa i higieny pracy (BHP); z zasadami ubezpieczania i ochrony praw pracowniczych; nabycie umiejętności wykonywania pracy; postępowania w sytuacjach awaryjnych oraz udzielania pomocy osobie, która uległa wypadkowi; zapoznanie z zagrożeniami w czasie pracy, stażu lub praktyki przy urządzeniach podlegających dozorowi technicznemu, urządzeniach i instalacjach energetycznych oraz urządzeniami górniczymi; nabycie umiejętności postępowania w razie wypadku, pożaru i w sytuacjach zagrożeń, w tym również nabycie umiejętności praktycznych. (*abc*)

(inf. http://centrala.enot.pl/aktualnosci/5.03.2016)

Konferencja Nitrogen + Syngas'2016 w Berlinie

W dniach 29.02.-03.03.2016 r. w Berlinie odbyła się 29 konferencja Nitrogen + Syngas 2016 – wiodąca w branży azotowej impreza o charakterze technicznym. Podczas konferencji zaprezentowano najnowsze rozwiązania technologiczne, trendy rynkowe i nowe inwestycje. Tegoroczna edycja konferencji przyciągnęła rekordową liczbę uczestników – 730 osób z ponad 50 krajów świata, w tym prawie 70 wystawców. *(kk)*

(http://www.ins.pulawy.pl/, 9.03.2016)