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WASTEWATER TREATMENT MODELS IN TEXTILE INDUSTRY

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Abstract. *Textile industry is a complex technological system that consists of a large number of operations and processes, such as production of raw materials, spinning, knitting, weaving, dyeing, etc. The technological processes of this industry use large quantities of water, resulting in the production of wastewater containing different kinds of colors and chemicals which have negative effects on the environment. The traditional wastewater treatment in textile industry has not given satisfying results and this is why it is necessary to look for alternative ways which will, firstly, reduce pollution, secondly, reduce pollution in the permissible range combining different methods in additions to using agents, and, finally, eliminate pollution completely. The purpose of this paper is to analyze the qualitative composition of the wastewater in textile industry and propose a wastewater treatment system with greater purification effect.*

Key words: *textile industry, wastewater, environmental pollution.*

1. INTRODUCTION

Textile industry is the world leader in the production of wastewater because water is an important raw material for different processes and operations. In the initial phase of textile processing, different kinds of impurities are removed, such as grease and starch, and various soaps and other agents that become parts of wastewater are used [1,2]. However, the greatest amount of pollution comes from wastewater made in the process of textile material dyeing, because color absorbs and reflects the sunlight, which increases the amount of bacteria to the level of insufficient biological degradation of impurities in the water, leading to the disturbance in ecological balance [3]. Colors can cause problems in many ways, such as acute and/or chronic effects on the exposed organisms, depending on the time of exposure

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and color concentration. Furthermore, colors have sufficient stability when exposed to light or oxidation agents.

Water pollution in textile industry is primarily caused by impurities which are isolated during textile finishing, and chemicals used in technological processes after finishing and rinsing. The characterization of wastewaters is made based on chemical analysis, together with optimal purification process.

The most significant level of pollution comes from cotton finishing processes, such as washing, scouring, bleaching, chemical bleaching, dyeing, printing and rinsing. Chemical and biological oxygen consumption, HPK i BPK5 in mg O_2/l, grows with the increase of the wastewater pollution.

Toxic metals, such as As, Pb, Cd, Cr, Co, Cu, Ni, Hg, can additionally affect wastewaters during the textile material processing and finishing [5]. Toxic metals in textile materials present the crucial problem for the environment and can be potentially dangerous for people's health. They are used in textile industry as oxidants, colors and means of consistency improvement. Considering the fact that the negative effects of toxic metals on people's health are widely known, it is necessary to control their concentration during the production and processing of textile materials [6]. They can be detected in wastewaters using chromatographic, spectrometric and electrochemical methods.

Nonmetals can be found in agents used for preprocessing and post - processing and their part in pollution is negligible, unlike tensides and their degradation products.

The expansion of textile industry has intensified the use of synthetic colors, which resulted in the increasing environmental pollution [7]. According to estimates, 800,000 tons of certified colors have been made [8], and until the end of the 19th century over 10,000 synthetic colors used in productive purposes have been developed [9].

Small amounts of color (less than 1 ppm for some colors) can cause a visible change in water color [10], which affects the aesthetic and transparency aspects of water, as well as possible ecological problems, such as toxic, cancerous or mutagenic effects [11].

Two most widespread groups of colors in textile industry are azo and anthraquinone colors [12].

Azo colors were used for textile dyeing, especially for cotton. However, because of high level of toxicity their use has decreased. Azo colors are susceptible to bioaccumulation and they are a threat to water life because of their allergic, cancerous, teratogenic and mutagenic characteristics. Physicochemical methods of their removal are not economical, as well as the need for disposal of harmful sludge, or the making of toxic compounds during the process of degradation. On the other hand, biological methods for wastewater discoloring are more economical and more frequently used.

Anthraquinone colors present the second class of textile colors and they are intensively used in textile industry. Reactive colors are not easily removed using typical wastewater treatment processes, and high concentration is typical for the dyeing process, making the treatment process more difficult [13].

From the environment protection aspect, the conditions for wastewater discharge are becoming more and more complex, and this is why the research in the area of wastewater treatment is going towards more frequent use of natural materials, primarily zeolite, mainly because of its effectiveness, but also because of its economy. The composition of textile wastewater depends on the type of colors used and additional agents contributing to organic wastewater pollution, and their main characteristic is poor chemical and biological oxidation, and therefore, discoloration. Coloration is stronger if the dyeing bath exhaustion is not high.

Usually, those are clear waters smelling of chemicals and containing fiber fragments. There is little suspended matter, and it is mostly organic (fiber fragments). Wastewater coming from the dying of textile fibers of this quality presents a great danger for the environment, making their treatment both a scientific and a social imperative. Legislation concerning color removal from industrial wastewater is becoming stricter in most of developed countries.

Environment protection in Europe is promoting the prevention of problems concerning pollution transfer from one part of the environment to another, meaning that most of the textile industries have developed, in their facilities, objects for wastewater treatment before releasing them into the recipient. Conventional processes, such as coagulation, flocculation, membrane separation, activated charcoal and biological methods used for effluent discoloration, containing reactive colors, cannot achieve adequate color removal. Also, most of these techniques used only physical transfer to remove colors from the wastewater phase into sludge, which needs further treatment before disposal. So far, research has shown that there is no universal treatment for this type of wastewater, but it is necessary to combine different processes which will be technically possible, and at the same time economically justified.

2. Qualitative Analysis of Textile Industry Wastewater

The analysis of relevant pollutants in wastewater is done twice a year, and sampling is done from each drain (maximum number of drains is 10). The parameters that are determined in wastewater are pH, dry residue, loss after annealing, total organic nitrogen, HPK from $KMnO_4$ and 20°CBPK$_5$,mg O_2/l [14].

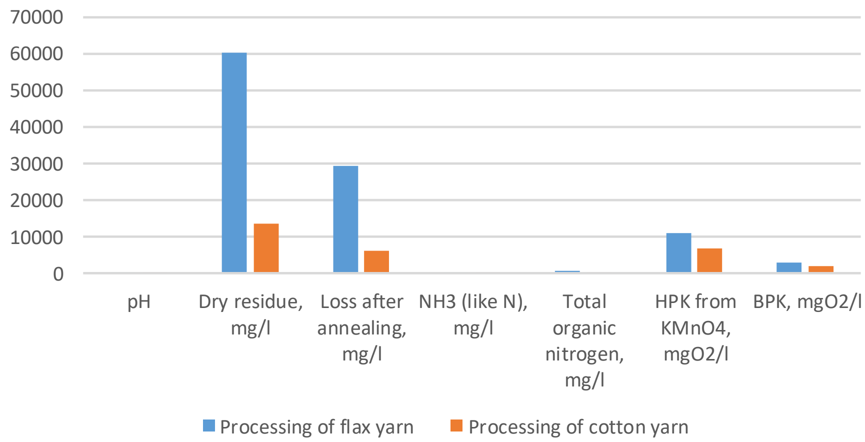

Fig.1 Concentration of relevant pollutants in wastewater, lye, made after scouring of flax cotton yarn [14]

Considering the fact that textile industry uses large amounts of water and includes the addition of a large spectrum of colors and chemicals, the chemical composition of effluents has become a real challenge from the aspect of the environment. Textile industry has a great influence on the environment, starting from extensive water usage (80-100 m^3/t of textile), wastewater release (115-175 kg COD/t of finished product), large amounts of organic chemicals used and low biodegradability [15]. Typical parameter values of textile industry wastewater include the following: HPK (150-12000 mg/l), suspended matter (2900-3100 mg/l), Kjeldahl nitrogen (70-80 mg/l) and BPK (80-6000 mg/l), where the ratio BPK/HPK around 0.25 points to the high content of non – biodegradable organic matter. Also, heat, acidity, alkalinity, and the presence of other organic pollutants in these effluents present an additional problem.

Textile industry wastewater, containing a complex mixture of chemicals and colors, can be extremely harmful for the environment if they are released into watercourse without proper purification treatment [16]. In addition, it has been proven that some colors and substances made in the process of their decomposition are toxic for the water life (water plants, microorganisms, fish and mammals) [17,18]. Moreover, it has been proven in a large number of studies that this kind of allergens can be susceptible to chemical and biological assimilation, cause eutrophication, consume dissolved oxygen, stop the filling of watercourses with oxygen, and have a tendency to separate metal ions, thus increasing genotoxicity and micro toxicity [19].

Intensive coloring coming from the presence of different types of colors presents a special problem in wastewater purification. Color removal either by coagulation, adsorption, or oxidation is connected with great difficulties and high exploitation expenses. Aluminum - sulphate, ferrous sulphate, ferric chloride and others are usually used as coagulants and $Ca(OH)_2$ and H_2SO_4 as agents for setting the optimal pH value of wastewater. Flocculants are added to accelerate the separation of the solid and liquid phases in wastewater purification (water – soluble natural or synthetic macromolecular compounds). The type and necessary amount of coagulants and flocculants, as well as optimal isoelectric point are experimentally determined for every specific wastewater from the dyeing process. The results of this type of studies often show that there is a synergic functioning of coagulants and flocculants, so that smaller amounts can be dosed, significantly decreasing purification expenses.

An unconventional and very effective approach to the removal of relevant colors is using synthetized clay - hydroxide sorbent based on bentonite and magnesium hydroxide. The experiment was done as follows: magnesium hydroxide is obtained by deposition of the 1 mole solution of magnesium sulphate and 1 mole solution of sodium hydroxide on pH=12 to 12.5. Bentonite is added to the residue obtained. Sorption properties of $Mg(OH)_2$ have been studied with bentonite content of 5 %, 10 % i 15 %. Relevant colors used in textile industry were used: sulphuric acid blue, Chlorantinlichat Blau 3RLL, indigo carmine, methylene blue and methylene violet. The studies were conducted during continuous stirring and the liquid and solid phases were separated by centrifugation. Discoloration efficiency was checked by UV-VIS spectrometry.

In order to determine the necessary duration of contact (which defines the volume of the reactor for color removal in the technological scheme of the facility) experiments were done and clay - hydroxide sorbent with 5% bentonite content was used, as well as solutions of different colors with the initial concentration of 100 mg/l.

It can be noticed from the table 1. that the basic amount of color is separated in the first 5 – 10 minutes, and the adsorption balance is reached after approximately 15 minutes. Further increasing of contact duration leads to the increasing of the purification degree, and in some cases the desorption of color particles can be seen, which is the reason why further experiments were done with contact duration of 15 minutes.

Table 1 The relationship between sorbed amount of color and contact duration, and sorption property of tested samples at different initial concentration of the final solution [14]

Type of color	Contact duration (min)	Sorbed amount of color (mg/l)	Color concentration in the solution (mg/l)	Bentonite content in $Mg(OH)_2$ (%)	Sorbed amount of color (mg/l)
Sulphuric acid blue	5	37,7	100		59,9
	10	51,3	400	5	64,3
	15	58,9	1000		69,0
Chlorantinlichat Blau 3RLL	5	42,3	100		63,7
	10	54,7	400	5	71,3
	15	63,7	1000		75,1
Indigo carmine	5	40,2	100		59,4
	10	51,9	400	5	65,2
	15	59,4	1000		70,3
Methylene blue	5	32,4	100		45,6
	10	39,5	400	5	54,2
	15	45,6	1000		65,8
Methylene violet	5	31,7	100		43,9
	10	38,7	400	5	53,8
	15	43,9	1000		63,2

Experiments were done for the sorption capacity of magnesium hydroxide, with bentonite content of 0 %, 5 %, 10 % and 15 % and the concentration of the corresponding colors from 100 to 1000 mg/l. Through the interpreting of the study results it was found that the cations of methylene blue and methylene violet linger over $Mg(OH)_2$ less than color anions. The addition of bentonite leads to the increased amount of sorbed color, because this increase is more important for color cations. The capacity of clay - hydroxide sorbents with bentonite content of 5% and 15% compared to methylene blue and methylene violet is 2 and 3.5 times bigger than magnesium hydroxide capacity, which does not contain bentonite. This could be the result of adsorption through bentonite, when the presence of uncompensated negative charge in the structure of montmorillonite, which is contained in bentonite and the process of ionic exchange between colors and ionic exchange of minerals.

Taking into account the fact that color concentration in textile industry wastewater usually does not go over 100 mg/l, experiments for solution purification were done with this concentration, using sorbent with bentonite content of 5% and different sorbent loss.

Clay - hydroxide sorbent based on bentonite and magnesium hydroxide can be successfully and economically used for textile industry wastewater treatment.

3. Textile Industry Wastewater Treatment

Different traditional techniques are used in the treatment of industrial wastewater containing colors, such as coagulation/flocculation, removal using membranes (ultrafiltration, reverse osmosis) or adsorption on active charcoal. However, their use as nondestructive methods can, as a consequence, have the forming of secondary pollutants. The biological treatment of this kind of wastewater in many cases is not regarded as a complete solution because of the resistance of certain types of colors to this kind of treatment. Organic matter in wastewater which cannot be easily destroyed in biological or conventional way are mostly treated by incineration, catalytic wet oxidation, catalysis in supercritical conditions, using sodium hydroxide in high temperatures and pressure, high – temperature reduction with hydrogen and oxidation by ruthenium tetroxide [20].

However, the incineration of organic waste can cause emission problems, unless the incineration conditions are not strictly controlled. Supercritical and wet oxidations are more perspective alternatives compared to incineration, but high expenses on the techniques of supercritical and wet oxidation make them less attractive for industrial use. Due to the stability of colors, their destruction is difficult to achieve and certain conditions have to be fulfilled, as well as searching for new, clean and cheap technologies in order to remove these compounds. During the last 20 years, the use of clean oxidants, such as O_3 and H_2O_2 has been widespread. The reason for their popularity is the fact they are well – accepted by the environment and the reactions that they participate in can be so projected as to be done in mild conditions. In the wastewater treatment that is done successfully, every non – organic residue has to be harmless, and the organic content of the solution has to be converted into CO_2, or a compound acceptable for biological treatment. In these conditions, O_3 and H_2O_2 are ideal because they do not lead to the production of nonorganic residue. More than one century ago, it was discovered that the dissolved iron ions strongly catalyze the oxidation of maleic acid using H_2O_2. Almost 40 years have passed since then, while more attention has been given to homogeneous catalytic reaction. Many experiments have been done since then in order to clarify the mechanism of catalysis and to apply generated hydroxyl radicals in the effluent treatment in textile industry.

Advanced oxidation processes have shown the biggest potential in the treatment of wastewater containing persistent and toxic substances. Among these processes, Fenton's procedure is well - known and successful in the treatment of effluents coming from the dyeing process and it presents the more economical and simpler option, compared to other advanced oxidation processes [22]. The scheme of Fenton's oxidation process is shown in Figure 2.

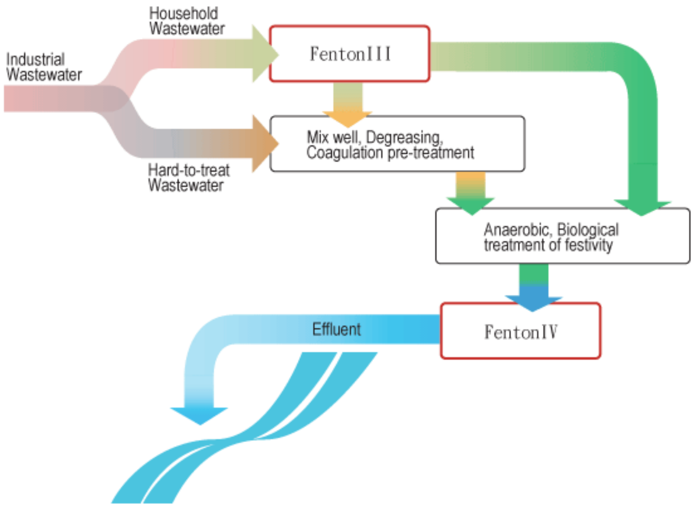

Fig. 2 Fenton's oxidation process

The redesign of technological production processes in textile industry includes the installation of the equipment for water purification and recirculation, as well as raw goods regeneration. For example, by extraction using solvents, such as carbon tetrachloride or benzene, lanolin from the wool washing wastewater is regenerated. During this process 20°CBPK5 is decreased by 20 – 30%. If the washing of wool is done by countercurrent procedure, it is possible to keep this concentration of potassium salts of fatty acids in the solution that it becomes economical to do their regeneration by evaporation and crystallization . Moreover, by the application of reversed osmosis, 90% of the wastewater from the dyeing process can be recirculated, while at the same time completely removing color (99%). Also, concentrated color is used again in textile fiber processing.

The technological schemes of the wastewater treatment facilities that are applied will depend on the required degree of purification required, that is, the removal effect that should be achieved on relevant pollutants.

The first purification phase of textile industry wastewater, after mechanical filtration through fine grids, consists of collection and equalization of qualitative and quantitative characteristics of waste streams in equalization tanks. One waste stream can be neutralized by another during this process, as well as partial coagulation with flocculation and discoloration, especially if the wastewater from the bleaching process contains excess oxidants. The volume of equalization tanks is usually equal to a four – hour or eight – hour wastewater flow.

Primary deposition shows insufficient wastewater purification effect because of the high concentration of surfactants (detergents). Because of the change in surface water charge, as well as dispersing effect, detergents inhibit the flocculation of color and other substances in wastewater and they slow down the deposition of suspended matter. Depending on the characteristics of wastewater and the nature of the present pollution stimulated by the primary deposition, the intensity of coloration can be reduced by 20 – 30% and the concentration of suspended matter by 30 – 35%, while the amount of residue is 0.3-1.3 %, relative to the quantity of water.

Considering the influence that surfactants have on the process of purification by chemical (coagulation and flocculation) and biochemical treatment (activated sludge) and the final effects of purification, it is very important to decrease the amount of surfactants in wastewater first. One of the most efficient operations in this phase of purification is flotation. The efficiency of removing surfactants by using flotation depends primarily on the degree of air dispersion, the duration of flotation and the air flow. Apart from surfactants, flotation can remove suspended matter (usually textile fiber) with the effect of 70%.

Oxidation using chlorine is partly undesirable, because it can produce toxic organochlorine compounds. Chemical reduction is used in order to increase the adsorption capacity of active charcoal. Azo colors can be decomposed by anaerobic biodegradation, whereby the coloration of wastewater is decreased. Active charcoal is mostly used as adsorbent in adsorption processes. Depending on the type of active charcoal and the type of color, adsorption capacities vary within wide limits – for acidic color 83 mg/g, and for base 385 mg/g. There is a tendency of replacing active charcoal with cheaper adsorbents, such as: natural aluminum silicate, tree bark, peat, etc.

During the conventional textile industry wastewater treatment, it has been found that throughout coagulation and flocculation processes color molecules partially bind to the particles of hydroxides of iron and aluminum, and are partially coagulated and deposited together with the solid phase.

Principal technological scheme of the facility for pretreatment of aggregated wastewater from textile industry is shown in Figure 3.

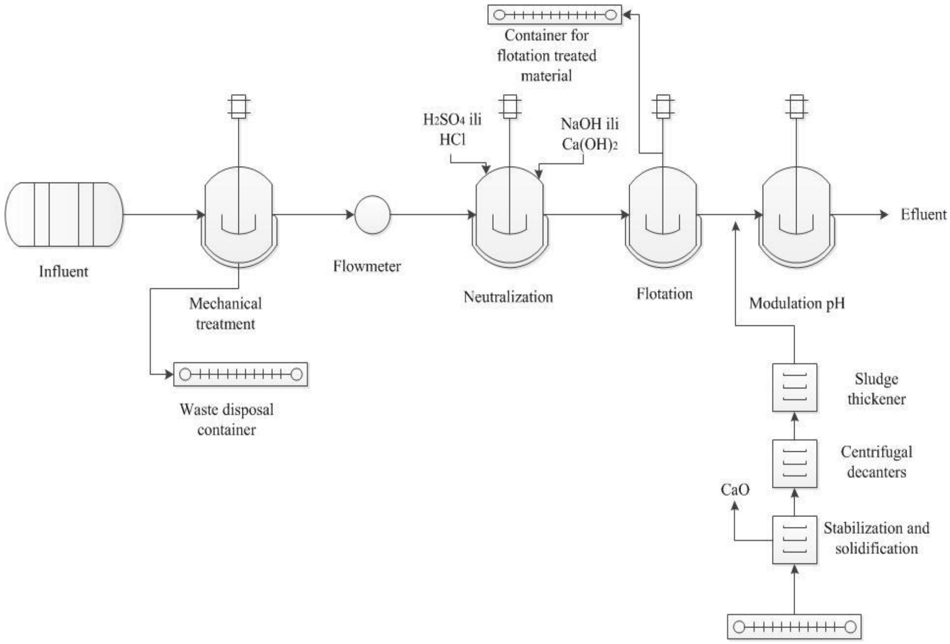

Fig. 3 Principal technological scheme of the facility for pretreatment of aggregated wastewater from textile industry

The use of ozonation, which is applied in the entire textile industry of the USA, where complete recirculation of water in the technological process is done, is very interesting. The influence of pH on the ozone oxidation reaction is negligible and this is why it is suitable for the purification of used color solutions and wastewater coming from rinsing. Ozonation is an expensive investment and causes a lot of problems during exploitation.

Although the economic effect is important in the process of choosing a system for wastewater treatment, before starting the purification of textile industry wastewater, all the possible pollution reductions in waste watercourses should be used, together with the decrease in water usage. First of all, possible changes in the process of textile materials (redesign of the technological production processes) should be considered. This can be done through:

- replacing the wet processing operations with dry ones,
- replacing chemicals with other chemicals containing lower organic pollution (HPK and 20°CBPK5), or being less toxic,
- regeneration of alkaline solutions,
- regeneration of additives and useful by-products,
- recirculation of less polluted rinsing wastewaters and
- replacing direct rinsing with countercurrent rinsing.

4. CONCLUSION

Considering the fact that textile industry is one of the major environmental pollutants, new legislation and norms have been adopted in accordance with the laws of the European Union. This is primarily related to water protection, which is polluted in the processes of finishing, processing and dyeing of textile materials. As conventional procedures of textile industry wastewater purification have not given satisfactory results, alternative procedures that use unconventional systems, putting the pollution level within the legally permissible scope, are listed in this paper.

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MODELI PREČIŠĆAVANJA OTPADNIH VODA TEKSTILNE INDUSTRIJE

Tekstilna industrija je kompleksan tehnološki sistem sastavljen od velikog broja operacija i procesa, kao što su izrada sirovina, predenje, pletenje, tkanje, bojenje i dr. S obzirom da tehnološki procesi ove industrije zahteva upotrebu velike količine vode, kao posledica nastaju otpadne vode koje sadrže različite vrste boja i hemikalija koje negativno utiču na životnu sredinu. Tradicionalnim načinom prečišćavanja otpadnih voda tekstilne idustrije ne dobijaju se zadovoljavajući rezultati, zato je potrebno tražiti alternativne načine koji će, najpre, dovesti do redukcije zagađenja, zatim do smanjenja nivoa zagađenja u dozvoljenom opsegu, kombinacijom različitih vrsta metoda, uz korišćenje agenasa, a potom do njegove potpune eliminacije. U tom smislu, cilj rada je analiza kvalitativnog sastava otpadnih voda tekstilne industrije i predlog sistema za tretman otpadnih voda koji ostvaruje veću efikasnost prečišćavanja.

Ključne reči*: tekstilna idustrija, otpadne vode, zagađenje životne sredine.*