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THE EXAMINATION OF THE MOST IMPORTANT QUALITY PARAMETERS OF WASTEWATER FROM CELLULOSE AND PAPER INDUSTRY AND ITS INFLUENCE AT SURFACE WATER RECIPIENT

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ABSTRACT

Basic raw materials for paper production are cellulose fibers and water. Water plays a major role in the process of cellulose and paper production and it is present in almost all phases of the cellulose fiber production process. Because of that the cellulose and paper industry is considered to be one of the largest consumers of natural resource polluters. In the paper are analyzed the following quality parameters of wastewater generated in cellulose and paper factory and discharged into a surface water recipient: temperature, pH value, electroconductivity, chemical oxygen demand (COD), biological oxygen demand (BOD_5), the share of biodegradable matter in total content of organic matter (BOD_5/COD) and the content of dissolved oxygen (DO). The aim of the study was to determine whether the values of the mentioned parameters are within the legally permitted limits and then to determine whether wastewater from the cellulose and paper industry influence a surface water recipient, or a living world in it. Analyzed wastewater samples were taken in the cellulose and paper factory "Natron Hayat", Maglaj. Wastewater from the cellulose and paper factory "Natron Hayat", Maglaj is discharged into the surface water recipient, the river Bosna.

1. INTRODUCTION

Wastewater means, in a wider sense, any water that has changed its physical, chemical and biological characteristics to a greater or lesser extent after it was being used [1]. Industrial wastewater is generated in factories and industrial plants after it is used in the production process or washing of certain technological equipment and workspace. Depending on the application of water in the production process and the production character, the level of wastewaterpollution is different, as it is different character of the pollutionpresent in that water. Pollution that is found in industrial wastewater can be: products of production, by-products that result from chemical reactions and various residues. Depending on the composition of the admixture and the specificity of their effect on the recipients, industrial wastewater is divided into [2]:

- water containing admixtures with specific toxic properties,
- water with inorganic admixtures that don't have toxic effects – this water is often not particularly hazardous to recipients, but contribute to the formation of sediments, reduces the water translucency, which can have a negative impact on the life of aquatic organisms,

- water with non-toxic organic matter - organic substances found in this water are decomposed biochemically and affect the increase of biological oxygen demand, lower the content of dissolved oxygen and reduce water transparency and
- water containing organic matter with specific toxic properties.

The wastewater from the cellulose and paper industry contains chemicals used in the process of obtaining paper, small pieces of wood, cellulose fibers, which, if not removed, can be caught for fish gills, melted lignin from wood, sulfur compounds and large amounts of organic pollution. Wastewater, also contains a large amount of solids, which if not purified and released into rivers, quickly overlap the bottom of the river destroying the fish and aquatic world that depends on food from the bottom of the river [2]. In the cellulose and paper industry there is black and white wastewater. Black wastewater originates from the cellulose production process. It is dark brown and the coloration is a consequence of the lignin presence, and this color affects the aquatic plantsphotosynthesis process. The water from the paper sector is called white water. The black and white wastewater are drained off by a collecting channel to the purification plant and then discharged into a surface water recipient. The amount of wastewater discharged into the surface water recipient can vary in a wide range. Particularly interesting is the so-called impact discharge of wastewater, which means the discharge of a larger amount of wastewater in relatively short time.

The harmful effect of polluting substances in wastewater is usually viewed from three aspects [2]:

1. impact on wastewater treatment,
2. impact on water recipients and
3. impact on the drainage system.

Biological oxygen demand, chemical oxygen demand and dissolved oxygen content are the most common criteria for wastewater pollution. Pollution criteria are used to assess the impact of wastewater on the surface water recipient, i.e. to estimate the damage that the untreated wastewater would cause in the recipient [3].

2. EXPERIMENTAL PART

Wastewater samples for conducting the experimental part were taken once a week, in a period of one month, in the cellulose and paper factory „Natron Hayat“, Maglaj. Samples were analyzed at the Metallurgical Institute „Kemal Kapetanović“in Zenica, in metallurgical chemistry department.

The experimental part contained the following steps:

1. Determination of sampling sites.
2. Sampling – wastewater sampling at the entry into the purification plant (unpurified wastewater) to determine the quality or degree of wastewater contamination from the cellulose and paper factory „Natron Hayat“, Maglaj and to asess the damage that unpurified wastewater would cause in the recipient. Then, wastewater samples were taken after purification (purified wastewater) to determine the quality of wastewater and to estimate the effects of wastewater produced in the factory„Natron Hayat,“ Maglaj, on the surface water recipient, the river Bosna.
3. Analysis of samples and testing the most important parameters of wastewater quality: temperature, pH, electroconductivity, chemical oxygen demand, biological oxygen

demand, the proportion of biodegradable substances in total organic matter content (BOD_5/COD) and dissolved oxygen content.
4. Analysis of the obtained values of the examined parameters and making the appropriate conclusions.

2.1. Analyzed parameters and examination methods

Figure 1 shows sampling sites in the wastewater treatment plant.

a) b)

Figure 1. The sampling places of wastewater: a) at the entrance to the treatment plant; b) the output of purified wastewater into the river Bosna [4]

COD is chemical oxygen quantity demanded for organic compounds oxidation and part of inorganic salts, and it is expressed as mg/dm^3O_2. COD was examined according to the standard JUS H.Z1.160 [4]. It is based on heating a sample at boiling temperature with a strongly acidic solution of dichromate in the presence of a catalyst Ag_2SO_4. The dichromate is added to the excess and the unused portion is determined by titration with a standard solution of fero ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$). The amount of dichromate consumed is calculated as the equivalent of the oxygen intake. Dichromate is reduced to equation [4]:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (1)$$

$HgSO_4$ is added, which prevents oxidation of chloride ion into chloride.

According to the regulation on conditions for discharging wastewater into the environment and the public sewage system of Federation Bosnia and Herzegovina the limit value of parameter COD of the wastewater that is discharged into surface water recipients is 125 mg/dm^3O_2 [5].

BOD is the amount of oxygen necessary to the water sample microorganisms under aerobic conditions at a temperature of 20 °C for a certain time period of incubation, to oxidize the organic matter in water. It was adopted that the incubation period for standard BOD determination is 5 days, at which time, at a temperature of 20 °C, it is oxidized 60-70% of originally present organic matter (BOD_5) [3]. The BOD is also the basic indicator that serves as an indicator of the impacts of wastewater on the receiver water where the oxygen content is reduced. As a rule applies, that during the determination of the degree of purification of polluted water at the plants it is necessary to achieve in the effluent such a BOD value that will not reduce the dissolved oxygen content downstream in the watercourse. For determination of BOD_5 manometer method and device BOD SYSTEM Oxidirect, Lovibond, shown in Figure 2 isused according to manual that comes with the instrument.

Figure 2. Device for BOD_5 determination, BOD OXIDIRECT, LOVIBOND [6]

According to the regulation on conditions for discharging wastewater into the environment and the public sewage system of Federation Bosnia and Hercegovina the limit value of parameter BOD_5 of the wastewater that is discharged into surface water recipients is 25 mg/dm^3O_2 [5].

Then the ratio BOD_5/COD was established. The presence of biologically non-biodegradable substances in wastewater is manifested by COD's higher value in relation to BOD. Biodegradability can be defined by the BOD_5/COD ratio. If this ratio tends to value zero, that means that it is difficult microbiologically degradable wastewater pollution, and if this relationship tends value one then it is a easy biodegradable microbiological pollution.

Temperature, pH, electroconductivity and dissolved oxygen content in the water sample were determined on the Sensodirect 150 set pH/con/oxy temperature, Lovibond (Figure 3).

Figure 3. Sensodirect 150 set pH/con/oxi/ temperatura, Lovibond [7]

At higher water temperatures, the metabolism of living organisms accelerates, oxygen will be consumed faster and the solubility of important gases will be decreased, such as oxygen, and also water density and viscosity will be decreased. Therefore, by changing the living conditions of the habitat, gradually will disappear organisms that need more oxygen and it will begin anaerobic decomposition of dead organic matter. According to the regulation on conditions for discharging wastewater into the environment and the public sewage system of Federation Bosnia and Hercegovina the limit value of the parameter "maximum temperature of technological wastewater" discharged into surface water recipient is 30 °C [5].
pH affects the chemical processes in the water and determines the structure of living communities. According to the regulation on conditions for discharging wastewater into the environment and the public sewage system of Federation Bosnia and Hercegovina the limit value of the the parameter "pH value of the technological wastewater" discharged into the surface water recipient is 6.5 – 9.0 [5].
Molecules of organic compounds, which do not dissociate in aqueous solution, conduct electricity very poorly (if at all). Most of the fresh and purified water has an electrical conductivity of 50 to 600 μS/cm.
The dissolved oxygen is the mass of oxygen molecules dissolved in the volume of water. Without enough oxygen, life in river is not possible for most plant and animal species. The

amount of dissolved oxygen below 3 mg/dm^3 is hazardous to most aquatic organisms and it is necessary to ensure that the wastewater discharged into rivers does not reach this value, so that there will be no deaths of the aquatic world at the site of pouring wastewater into the river [8].

3. RESULTS AND DISCUSION

In Table 1 are given the values of the analyzed parameters.

Table 1. Quality parameters of the examined wastewater at the entry into the purification plant (unpurified water) and before it was discharged into the river Bosna (purified water)[4]

Samples	*t (°C)*	*pH*	*electrocondutivity (µS/cm)*	*COD (mg/dm^{3}O$_2$)*	*BOD (mg/dm^{3}O$_2$)*	*BOD$_5$/ COD*	*DO (mg/dm^{3}O$_2$)*
S$_1$	40.7	7.68	608	903.24	172	0.190	2.3
S$_1$*	25.0	7.30	718	32.87	11	0.335	6.0
S$_2$	40.5	7.50	665	495.6	145	0.293	3.2
S$_2$*	25.0	7.46	747	37.18	11.5	0.309	6.0
S$_3$	37.8	7.60	682	1081.2	167.5	0.155	3.8
S$_3$*	25.6	7.15	850	65.96	13	0.197	5.9
S$_4$	35.4	7.20	743	417.99	185	0.443	4.4
S$_4$*	25.0	7.10	991	34.13	13	0.381	5.9
S$_5$	38.8	7.70	606	1353.47	192.5	0.142	3.9
S$_5$*	26.3	7.44	845	35.99	12	0.333	5.8

Legend: S – unpurified water; S - purified water*

The temperature of the wastewater which is discharged into water recipient satisfies a value set by the Regulation on conditions for discharge of the wastewater into surface water bodies, which is 30 °C. In Figure 4 it can be seen that the temperature values of unpurified waste water are high and reach 40.7 °C.

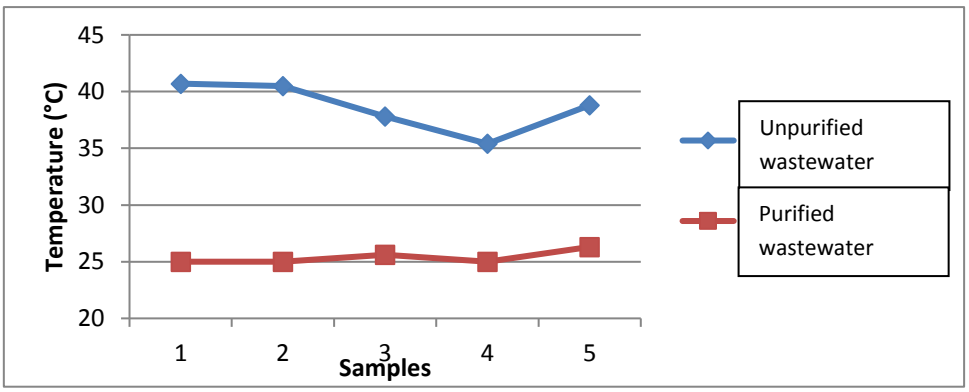

Figure 4. Temperature of unpurified and purified wastewater [4]

The pH of the purified wastewater which is discharged into surface water recipient satisfies a value set by the Regulation on conditions for discharge of the wastewater into surface water bodies, which is 6.5 - 9. In Figure 5 it can be seen that the pH values of the unpurified wastewater are within the permitted limits.

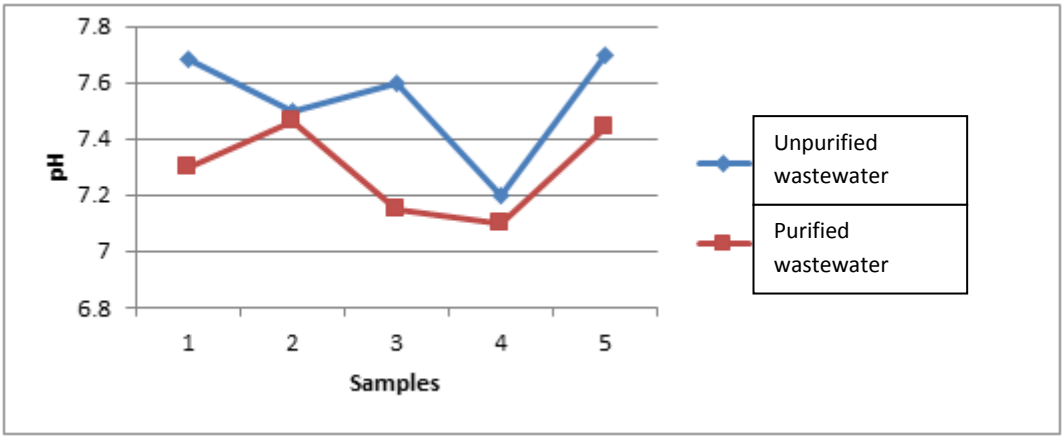

Figure 5. pH value of unpurified and purified wastewater [4]

Electroconductivity of unpurified wastewater ranges from 606 to 743 μS/cm and purified wastewater from 718 to 991 μS/cm. The values of electrical conductivity are not very high because it is a cellulose and paper factory, where the effluent is burdened with a lot of organic material that poorly or not conduct electricity. From Figure 6 it can be noticed that the electroconductivity of the wastewater that is discharged into the river Bosna is higher than unprocessed water, since it will be reduced the organic load of wastewater after purification which negatively influences the conductivity.

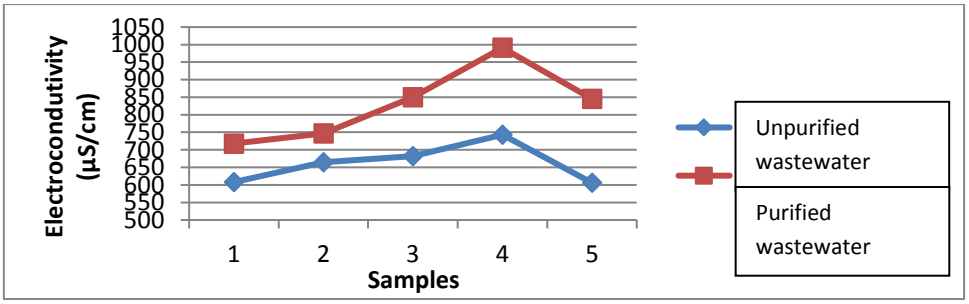

Figure 6. Electroconductivity of unpurified and purified wastewater [4]

In Figure 7 it can be seen that the value of COD of wastewater that will be discharged into a river Bosna is far below the limit set by the Regulation on conditions for discharge of the wastewater into surface water bodies, and amounts 125 mg/dm^3O_2 [5].

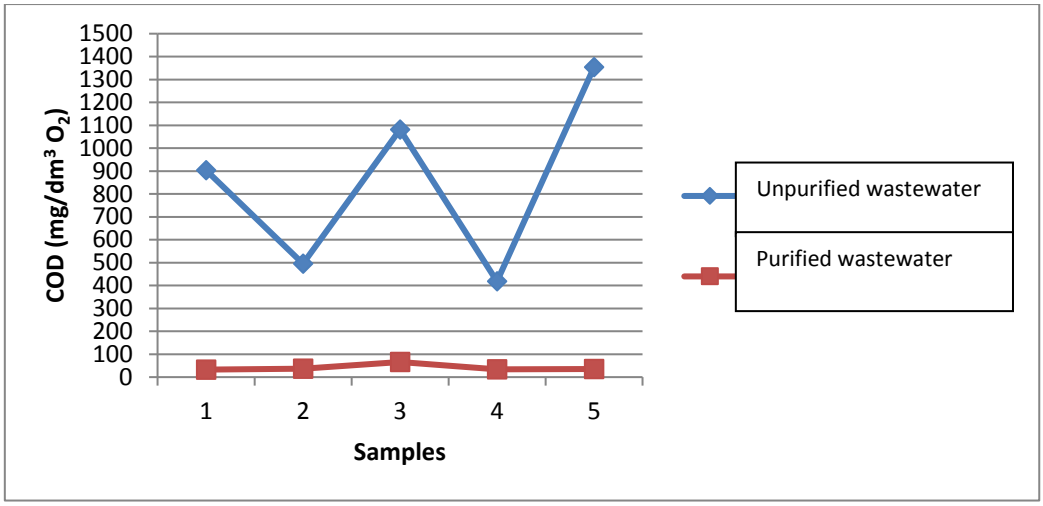

Figure 7. COD values of unpurified and purified wastewater [4]

Figure 8 shows the values of BOD_5 for unpurified and purified wastewater. Values of $BOD_5$of wastewater after purification are significantly reduced and these values are below the prescribed limit of 25 mg/dm^3O_2.

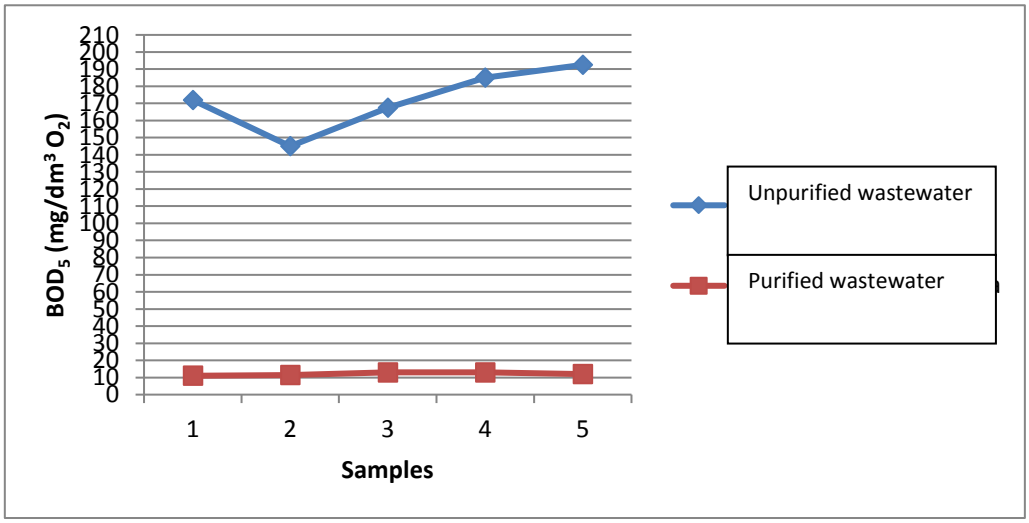

Figure 8. BOD values of unpurified and purified wastewater [4]

The BOD_5/COD ratio (table 1) amounts from 0.142 to 0.443, which indicates that wastewater from the cellulose and paper industry is loaded with organic hard biodegradable materials.

Figure 9 shows the values of dissolved oxygen in unpurified and purified water. Based on Figure 9 it can be concluded that the dissolved oxygen values in unpurified wastewaterare very low due to the large organic load of water. However, by purifying the wastewater values will become higher. The minimum value has a sample of purified wastewater 5, and amounts 5,8 mg/dm^3O_2. Wastewater from the cellulose and paper factory "Natron Hayat", Maglaj is discharged into the river Bosna, and the river Bosna belongs to III class according to the Regulation of categorization and classification of watercourses, where the content of dissolved oxygen reaches about 4 mg/dm^3.

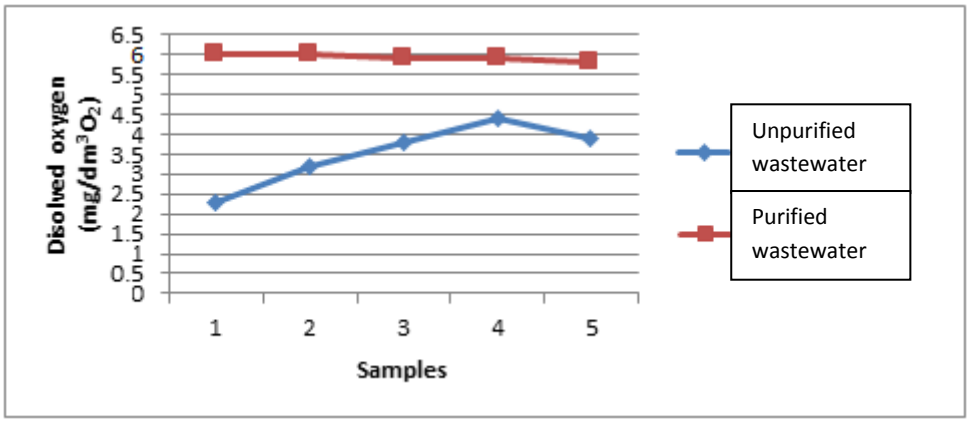

Figure 9. Dissolved oxygen values in unpurified and purified wastewater [4]

4. CONLUSION

Based on the obtained values of the analyzed parameters it can be concluded that the wastewater from the cellulose and paper industry that comes into the purification plant (unpurified water) is heavily loaded with organic pollution and if it would be directly discharged into the river Bosna as such would cause an ecological catastrophe. However, the wastewater that is being discharged into river Bosna after purification has a satisfactory quality and all the values of the examined parameters are within the legal limits. Based on this it can be concluded that wastewater from the cellulose and paper industry after it has been purified does not have negative impact on the surface water recipient and its living world. The wastewater from the cellulose and paper industry from the factory „Natron Hayat“, Maglaj, which is released into the river Bosna is wastewater that contains non-toxic organic matter in the legally permitted limits and will not negativelly affect the surface water recipient.

5. REFERENCES

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