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Technical Paper

The Cellulose and Paper Industry Wastewater Treatment

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Abstract: A large amount of water is used in the cellulose and paper industry, which causes the production and release of the industrial wastewater which can, due to the amount and loads of contaminants, significantly affect the quality of the water environment if the adequate meassures for the rational use and purification of the same are not implemented and continuously applied. These wastewaters have a large organic contamination (BOD5 and COD), a large sulphite concentration, phenol and tannin (lignin) and chemicals that are used in the process of cellulose and paper production. The treatment of the wastewater from the cellulose and paper production in "Natron–Hayat" Maglaj after the realization of the wastewater disposal project done in 2007 is analyzed in this paper. This company has accomplished the project of recovery and modernization of the wastewater purification system towards the rational use and efficient purification of the industrial waters. With the device efficiency analysis for the wastewater treatment it was concluded that the purification efficiency level is acceptable according to the emissions standards issued by the regulations for the terms of wastewater release into the natural recipients and public sewerage system. Thereby, this company has significantly contributed to the water resources protection, ie river Bosna, which is a recipient of the wastewaters released from this company's plant. However, it would be good to analyze the possibility of the optimization of this device in oreder of exploiting the biogas as a potential fuel, adn sludge as a potential fuel and for other purposes.

INTRODUCTION

A large amount of water is used in the cellulose and paper industry, because of the technological process' nature. This causes the production and release of the industrial wastewaters which can significantly affect the quality of the water envirnoment if adequate meassures for rational use and purification of the same are not implemented and continuously applied.

Wastewaters from the cellulose and paper industry have a large organic contamination (BOD_5 and COD), a large hazardous substances concentration: sulphites, phenol and tannin (lignin) from the wood and therefore must be purified before released into the recipient, especially if the recipient are surface waters (Stanisavljevic, Krstic, Takic, et al., 2011).

Wastewaters from the cellulose and paper industry contain chemicals which are used in the process of cellulose and paper production, small parts of tree crust and wood, cellulose fibers and dissolved lignin from the wood. The wastewater often has a dark brow colour and odor from the organic sulfur compuonds (mercaptan) and compounds added for wood protection (Tuhtar, 1990).

The treatment of the wastewater from the cellulose and paper production in „Natron – Hayat“ Maglaj after the realization of the wastewater disposal project done in 2007 is analyzed in this paper. This company has accomplished the project of recovery and modernization of the waste water purification system towards the rational use and efficient purification of the industrial waters. Thereby, this company has significantly contributed to the water resources protection, ie river Bosna, which is a recipient of the wastewaters released from this company's plant.

THE WASTEWATER CHARACTERISTICS IN THE CELLULOSE AND PAPER PRODUCTION PLANT OF THE „NATRON – HAYAT“ MAGLAJ COMPANY

The so called black wastewaters are produced during the cellulose production in the „Natron – Hayat“ Maglaj plant and the so called white wastewaters are produced during the paper production. Characteristics of these waters are given in Table 1.

Table 1: Industrial waste water characteristics.

Wastewater characteristics	Black wastewaters	White wastewaters	Characteristics of all wastewaters
Amount	18 000 m^3/day	22 000 m^3/day	40 000 m^3/day
Total BOD_5	7 000 - 12 000 kg/day	3 000 - 6 000 kg/day	10 000 - 18 000 kg/day
Total COD	14 000 - 35 000 kg/day	6 000 - 13 000 kg/day	20 000 - 48 000 kg/day
Total SM	3 500 - 7 000 kg/day	6 000 - 13 000 kg/day	9 500 - 20 000 kg/day
Maximal BOD_5 concentration	700 mg/l	350 mg/l	
Maximal COD concentration	2 000 mg/l	750 mg/l	
Maximal SM concentration	400 mg/l	750 mg/l	

All of the listed waste waters are led to the wastewater treatment plant, which characteristics are analyzed in this paper.

THE WASTEWATER TREATMENT DEVICES' CHARACTERISTICS IN THE „NATRON – HAYAT“ MAGLAJ

The wastewater treatment plant is concived as a physical, chemical and biological system for the waste water purification, that are again used in the technological pocesses (circular system), which provides a significant save and rational water use. The wastewater treatment process is shown in the Table 2 and in Figure 1.

Table 2:The operations of the wastewater purification device in the „Natron-Hayat“ Maglaj.

Previous treatment	Primary treatment	Secundary treatment	Tertiary treatment	Sludge treatment
Grille Equalisation	Dispersed substances removal: settling	Biodegradable substances removal: activated sludge procedure	Desinfection	Thickening and treatment on the belt presses

A large solid waste separated on the grille is disposed into the containers and the wastewater goes into the equlization tank where a mixing of wastewater with aluminum sulfate ($Al_2(SO_4)_3$ x $18H_2O$) is done. Aluminum sulfate affects the coagulation and settling. Also, a pH value adjustment is done in the equalization tank, ie a neutralization by automaticaly dispensing the NaOH or H_2SO_4. After that but before the primary clarifier an anionic polyelectrolyte is metered for faster settling in the primary clarifier.

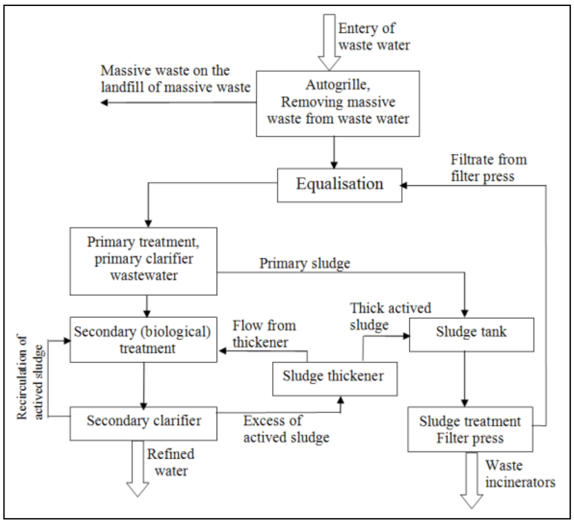

Figure 1: The wastewater treatment chart.

In the primary treatment, apropos in the primary clarifier the dispersed substances are removed. The antifoaming agents and sodium hypochlorite are added if needed, when a layer of foam starts to block the exchange of oxygen between the medium and air, therefore reducing the bio processes' efficiency. The water retention time is 2,4 hours. Around 500 m^3/day of sludge with the dry matter content around 4% is separated in this phase. The primary sludge is transported into the sludge tank via pumps. The primary clarifier waste waters go into the distribute pane where the needed chemicals are added (nutrients, antifoaming agents and ferric sulphate). The wastewater primary is shown treatment’s efficiency is shown in the Table 3.

Table 3: The effluent characteristics after the primary clarifier.

Wastewater characteristics	Amount	Reduction
Biological oxygen demand (BOD_5)	10 000 kg/day	44.4%
Chemical oxygen demand (COD)	30 000 kg/day	37.5%
Suspended matters (SM)	4 000 kg/day	80%

The primary clarifier wastewaters go into three aeration tanks in which the biological treatment is done by the activated sludge procedure. Oxygen is introduced into the tanks with simultaneous water mixing. Thereby, preventing the settling and accelerating the microorganisms' contact with the food, ie incoming content in terms of BOD, COD and SM. The mass of microorganisms goes with the wastewater into the additional settling tank. A part of microorganisms' mass from settled sludge (activated sludge) is brought back into the biological tank (return sludge). Rest of the sludge goes into treatment before the final disposal.

The oxygen supply is done by 3 compresors of total capacity of 19260 kg/day and 20 spiral aerators in the first aeration tank of total instaled power of 370 kW (20 pcs. x 18,5 kW), and also by membrane diffusor system in the second and third tank. The total capacity of oxygen influx is 28140 kgO_2/day. The disc type membrane diffusor (total 1800 pcs.) is used for the fine air bubble production to increase the oxygen transfer efficiency. The propeler mixers are instaled in the second and third aeration tank to prevent the forming of anaerobic conditions. This equipment works automaticaly depending on the meassured disolved oxygen concentration in the aeration tanks. The aeration tanks' oxygen concentration is monitored by three controllers (oximeter). In case of negative oxygen value one of the aerators or a compresor is activated to provide the oxygen.

The aeration tanks' wastewater goes into 3 secondary clarifiers through the distributional chamber. The secondary clarifiers' total volume is 6600 m^3. The secondary clarifiers purpose is to provide the microorganisms' settling which have envolved in the aeration tanks. For the microorganisms' evolvnig process a content in terms of BOD_5, COD and SM was used. The water retention time is 4 hours. In that time, the activated sludge is settling on the bottom of the tank and is collected with the chain scrapers. A part of the settled sludge is pumped on the begining of the biological process as a recirculated sludge, while the excess sludge is transported into the sludge thickener and then into the sludge tank. The amount of excess sludge is 1000 m^3/day.

After the biological treatment, the treated water has a following quality:

- BOD_5 < 25 mg/l,
- COD < 125 mg/l,
- SM <75 mg/l.

The wastewater testing before and after the biological phase is done in August 2012 to determin the biological treatment's efficiency. Obtained BOD_5, COD and SM values are given in the Table 4.

The table 4 data shows that all of the examined parameter values are lower than the defined limiting values of the qualitiy parameter emissions for the industrial wastewaters that are released into the surface waters. These emissions are issued by the regulations for the terms of wastewater release into the natural recipients and public sewerage system (c).

The BOD_5 is done every 5 days, thus it's value was meassured 4 times in the month of August, while COD and BOD were meassured 22 times which is the number of woking days in the month of August.

The BOD_5 average value before the biological treatment was 97,25 mg/l and after the biological treatment 19,125 mg/l.

The statistical efficiency of the BOD_5 removal is determined based on the ratio of the contamination indicators before and after the biological treatment (Imamovic, Goletic, and Ekinovic, 2010). Based on these two values the average degree of the BOD_5 removal efficiency is calculated:

$$\eta = \frac{97,25 - 19,125}{97,25} = 0,803$$

It follows that the BOD_5 removal efficiency is 80%, which is slightly lower than the values given by the BAT, which is 85–98 % (BAT).

Table 4: The wastewater analysis results before and after the biological treatment.

Date	BOD_5, mg/l		COD, mg/l		SM, mg/l	
	Before biologica treatment	After biological treatment	Before biological treatment	After biological treatment	Before biological treatment	After biologica treatmer
1.8.12			507	122	172	16
2.8.12			530	118	118	22
3.8.12			653	115	72	17
6.8.12	105	18	609	116	80	10
7.8.12			629	115	92	12
8.8.12			571	114	44	12
9.8.12			611	123	89	14
10.8.12			700	120	96	12
13.8.12			840	120	20	16
14.8.12			617	117	88	12
15.8.12	85	18,5	600	120	108	12
16.8.12			555	117	80	10
17.8.12			560	112	140	12
21.8.12			584	110	80	12
22.8.12	112	22	557	119	132	16
23.8.12			517	117	136	16
24.8.12			598	114	92	16
27.8.12			480	116	116	20
28.8.12			416	118	28	10
29.8.12	87	18	403	113	24	12
30.8.12			380	117	32	10
31.8.12			403	105	40	10
Average values	97.25	19.125	560	116.27	85.4	13.76

There are some other data in the references about the BOD_5 removal efficiency which varies between 70–90 % (Tadeschi, 1997).

The average value of COD before the bioogical treatment was 560 mg/l, and after the biological treatment 116,27 mg/l. Based on these two values a degree of the COD contamination removal efficiency is calculated:

$$\eta = \frac{560 - 116,27}{560} = 0,79$$

It follows that the degree of the COD removal efficiency is 79%.

The degree of the COD removal efficiency after the activated sludge procedure is 75% (Tadeschi, 1997) or 60 – 80% (BAT).

The SM average value before the biological treatment is 85,4 mg/l and after the biological treatment 16,59 mg/l. Based on these two values a degree of the SM removal efficiency is calculated:

$$\eta = \frac{85,4 - 13,59}{85,4} = 0,84$$

It follows that the degree of the SM removal efficiency in the bioogical treatment is 84%.

The SM removal efficiency after the biological treatment is 85–90 % (BAT, 1997). Also it is considered that activated sludge wastewater treatment has a SM reduction efficiency of 70–90 % (Simicic, 2002) or up to 95% (Tuhtar, 1990).

To perform the purification procedure efficiently, it is necessary to provide the food for the microorganisms, apropos the organic content in terms of BOD_5 or COD. There is a large chance of degradation at a lower organic matter concentration in the water, while the microorganisms activity is limited in case of a very high organic matter concentration in the water. Because of that it is important to establish the sludge content parameter which represents the ratio of the organic content and suspended matter and it is expressed by this equation

$$\frac{F}{M} = \frac{kgBPK_5}{kgSM}$$

The organic content to suspended matter ratio in particular case is F/M = 0,19–0,34 $kgBOD_5/kgSM$.

The references state the following data about the organic content and suspended matter ratio (Glancer-Soljan, 2001):

F/M = 0,5 – 5,0 – highly loaded activated sludge
F/M = 0,2 – 0,4 – medium loaded activated sludge
F/M = 0,1 - 0,2 - low loaded activated sludge.

With the comparative analysis of the organic content and suspended matter ratio in the wastewaters from the “Natron-Hayat“ Maglaj comany's plant with the references data it can be concluded that this sludge is medium loaded.

The medium loaded sludge (F/M = 0,2 – 0,4) can achive a large BOD_5 removal efficiency up to 95% (BAT).

According to the BAT the sludge load of F/M = 0,15 with the water retention time in the aeration tanks from 14 hours up to two days is considered an optimal menegament of the activated sludge procedure. A lower F/M ratio gives a better BOD_5 removal efficiency, but at the same time if this ratio is too low there can be certain problems like defloculation and dispersal, apropos the sludge expansion inside the secondary clarifiers and its flow with the efluent (Simicic, 2002).

This ratio can be corrected and maintained constant by performing the higher or lower return of the activated sludge from the additional clarifiers to the aeration tanks after the biological treatment.

Other parameters of the successful management of the activated sludge procedure, that are in direct relation with the sludge content are sludge settleability, sludge volume index and sludge age.

The sludge settleability in the analyzed device varies within the limits of 250 - 500 ml/l. This parameter depends on the primary wastewater treatment. The sludge settling has no optimal value but it varies from plant to plant, but the most important property of this patameter is sludge stability, because a slight change (like slidge rising) can cause some problems in the wastewater treatment technology.

The sludge volume index in the analyzed device is around 150 ml/g. According to the references, sludge index varies within the following limits (BAT):

- SVI ≈ 100 ml/g good quality sludge
- SVI = 80–140 ml/g fair quality sludge SVI > 150 ml/g poor quality sludge.

This parameter is also important in terms of sludge settleability.

Sludge age in the analyzed device is around 6–11 days. The sludge age is inversly proportioned to the F/M content. Larger F/M content gives a lower sludge age and vise vrsa. The optimization of these factors (sludge content, settleability, sludge volume index and sludge age) affects the wastewater treatment efficiency.

Addition to the above, for a efficient wastewater biological treatment process it is necessary to provide an optimal ratio of the nutrients for the system performances improvement and the micronutrients (copper, manganese, cobalt, selenium), which are not necessary.

The data of the obtained wastewaters' biological treatment efficiency degree values from the “Natron–Hayat“ Maglaj, and the values recommended by the BAT and the references (Tuhtar, 1990; Tadeschi, 1997; Simicic, 2002; Glancer-Soljan, 2001), are given in the Table 5.

Table 5: The comparative wastewater's biological treatment efficiency analysis.

Parameter	BOD_5	COD	SM
Natron-Hayat Maglaj	80 %	79 %	84 %
BAT	85–98 %	75–90 %	85–90 %
References	70–96 % to 95 % 70–90 %	> 75 %	70–90 % to 95 % 70–90 %

From the data given in the previous table it can be seen that BOD_5 removal efficiency is slightly lower than the BAT values but it is within the limits stated in the references. The COD and SM removal efficiency is within the limits stated in the BAT and in the references.

The primary and biological sludge is collected into the sludge tank from where it is transported to the dryin process via belt filter presses capacity of 70 m^3/h, 1400 kgSM/h. The presses filtrate goes into the equalisation tank for the inclusion into the purification process. To increasse the sludge drying process efficiency, the cation polyelectrolyte is introduced into the sludge. The dried sludge is now transported to the municipal landfills but the attempts are made to use it as an energy product for the industrial boiler or for other purposes.

The activated sludge procedure is widely used in the cellulose and paper production industry and it is used in 60–75% of the existing cellulose and paper production plants around the world (BAT).

The adctivated sludge procedure advantages are relatively high wastewater purification efficiency, possibility of process control (especially oxygen consumption control) and relatively small space demands. Disadvantages of this process are relatively high disturbance sensitivity during the process, high sludge production and relatively high operation expencess.

The tertiary treatment includes the effluent desinfection before its release into the river Bosna, which is the final recipient of the wastewaters from the mentioned company. Desinfection removes the pathogenic microorganisms.

The most economically justified way to treat the wastewaters with the high biodegradable organic content, as are the cellulose and paper industry wastewaters, is to treat them in two phases: anaerobic and aerobic, with the biogas production as a potential fuel. The anaerobic biological wastewater purification is a process which is energetically favorable, because it generates high energy value methane which can be used as the most environmentaly suitable fuel (Zarkovic, Krgovic, and Rajakovic, 2004; Avdic & Goletic, 2012).

CONCLUSIONS

The device efficiency analysis of the wastewater treatmen from the cellulose and paper production plant in the „Natron – Hayat“ Maglaj company led to conclusion that the purification efficiency degree is acceptable compared to the emissions standard issued by the regulations for the terms of the wastewater release into the natural recipients and public sewerage system.

The wastewater contaminating matter removal efficiency is satisfying. However, it would be good to analyze the possibility of the optimization of this device in order of exploiting the biogas as a potential fuel and sludge as a potential fuel and for other purposes.

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Summary/Sažetak

U industriji celuloze i papira koristi se velika količina vode, što uzrokuje nastanak i ispuštanje tehnoloških otpadnih voda koje zbog količine i opterećenja zagađujućim tvarima mogu značajno uticati na kvalitet vodnog okoliša ukoliko se ne primjene i kontinuirano ne provode adekvatne mjere za racionalno korištenje i prečišćavanje istih. Ove otpadne vode imaju veliko organsko zagađenje (BPK_5 i KPK), velike koncentracije sulfita, fenola i tanina (lignina) i kemikalije koje se upotrebljavaju u procesu dobijanja celuloze i papira. U ovom radu analizirana je obrada tehnoloških otpadnih voda iz proizvodnje celuloze i papira “Natron-Hayat“ Maglaj nakon realizacije projekta zbrinjavanja otpadnih voda izvedene 2007. godine. Ova kompanija je realizovala projekat sanacije i modernizacije sistema prečišćavanja otpadnih voda u cilju racionalnog korištenja i efikasnog prečišćavanja tehnoloških voda. Analizom efikasnosti uređaja za obradu otpadnih voda konstatovano je da je stepen efikasnosti prečišćavanja prihvatljiv u odnosu na emisione standarde propisane Uredbom o uvjetima ispuštanja otpadnih voda u prirodne recipijente i sistem javne kanalizacije. Time je ova kompanija značajno doprinijela zaštiti vodnih resursa, odnosno rijeke Bosne, koja predstavlja recipijent otpadnih voda ispuštenih iz pogona ove kompanije. Međutim, dobro bi bilo analizirati mogućnost optimizacije ovog uređaja u svrhu iskorištavanja bioplia kao potencijalnog goriva, te mulja kao potencijalnog goriva ili za druge svrhe.