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Use of Wetland for Dye-house Waste Waters Purifying Purposes

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Abstract: Textile finishing processes produce waste waters burdened by high amounts of dyestuff, which has not been chemically bonded to the fiber in the process of fixation. Also, a great threat to the inlet water ways and the environment itself are high quantities of salt (e.g. NaCl or Na_2SO_4), used in the processes of cotton dyeing. Although, recently more and more new physical and chemical purifying methods are being developed, with the emphasis on membrane processes, this paper revises an alternative solution to the problem, which is adapting and constructing a purifying system similar to the processes which have been occurring in the nature forever.

Efficiency of such constructed wetland will depend on selection and mass relation of natural adsorbents, which should correlate to the natural geological profiles. In this paper wetland was optimized within laboratory investigations and then used as an only method employed in order to purify dye-house wastewater. Optimized combination of purifying media along with Phragmites Australis achieved reduction of measured biological parameters (COD, BOD_5, TOC, AOX, el. conductivity, pH, NH_4^+, NO_3^-, NO_2^-, total P and the amount of Cl^- ions). In order to significantly reduce SAC values, another purifying method (e.g. chemical) should be employed.

Key words: Constructed wetland, waste water treatment, biological parameters, dye house waste waters.

Introduction

Wet processes employed in modern textile industry require water of very good quality concerning the amount of suspended solids, dyes or detergents. Also, legislation concerning ecology imposes great demands when discharge of toxic materials is in question, which means ensuring a better performance of water recycling. The emission of sewage from the communities, small industrial plants and dumping-sites has not been solved until today. Not before recently we recognized the real value of the wetland ecosystem also from the point of view of their self-clearing capacities. Therefore, development of alternative technologies as constructed wetlands (CW) for WWT (waste water treatment) was initiated (Bulc and Sajn-Slak, 2003; Sajn-Slak et al., 2005; Parac-Osterman et al., 2004). CWs have many advantages such as low construction and operation costs, simple installation and maintenance. CW are being used for both small and large applications. Variations of this technology are in use to deal with single-family residences to highway runoff, landfill sites, food processing industries, and settlements up to 1000 PE (Ojstrsek and Golob, 2004; Parac-Osterman and Durasevic, 2005; Parac-Osterman et al., 2003). On the basis of treatment efficiency, it is evident that the CW is ecologically acceptable small WWT technology. The idea of wastewater treatment in the lagoons with floating plants and later in the CW was born in the second half of the eighties.

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The experiences with floating plants showed that the CWs are more suitable than lagoons because of many reasons (cold winters, potential odours and insects, large areas needed). An experimental period of treating wastewater in CW followed. During this period exploration was based on experiences of some European researchers Kickuth and Clayton (Skelly, 2000; Golob et al., 2005; Parac-Osterman and Sutlovic, 2003; Mbuligwe, 2004). Later on systems were designed on the basis of hydraulic and pollution loads, and legislative regulations for discharging the effluent into the receiving waters. The media has an important role in treatment of wastewater; therefore different mixture in each system in accordance with organic loads was selected. The main attention was paid to prevent clogging. Theoretical hydraulic loading of media was in each case at least 10^{-3} m/s. The basic design criteria was based on a project started in 1991 in Austria by Urbanc and Bercic, which was modified through selection, application and comparison of various options in situ. After 1995 in the systems cleaning sumps and drainages, mechanical system for exchanged water flow in the vertical beds and combination between vertical and horizontal flow within one bed was introduced. Vertical and horizontal flow (VF, HSF) was examined in 10 systems. In others, which consist of one or more interconnected beds, the flow was horizontal. CWs were installed to treat sewage, landfill leachate, industrial wastewaters, motorway run-off (Parac-Osterman and Sutlovic, 2003; Mbuligwe, 2004; Brown, 1994).

A Wetland System for the purposes of Textina‘s textile factory dye-house waste waters purifying has been designed and constructed in Ajdovšèina, Slovenia. In this paper a laboratory optimizing of CW, Limnos (investigations carried out at Faculty of Textile Technology in Zagreb, Croatia and Faculty of Mechanical Engineering, University of Maribor, Slovenija – partners on Project Eureka Textilwet E!2983), employed for dye-house waste waters purifying processes is shown. Obtained results of the preliminary investigations directly influenced the design and construction of the pilot project. Also, in order of determining the efficiency of the process, two types of model dyestuff (mixture), belonging to reactive and vat group, were used.

This paper revises efficiency of aforesaid purifying system especially emphasizing broad spectrum of analytical methods used (Chih-Sheng and Shui-Ping, 2005; Dewick et al., 2004). Parameters measured and used for the evaluation of the waste water quality before and after the purifying process were COD, BOD_5, TOC, AOX, el. conductivity, pH, NH_4^+, NO_3^-, NO_2^-, total P, SAC and the amount of Cl^- ions. Obtained biological parameters are determined by and should be within the limits regulated through legislation.

Experimental

Construction of Wetland System

The pilot system was designed on the basis of hydraulic loads of one cubic metre per day and pollution loads, all in accordance with Slovenian regulations concerning the effluent discharges into the receiving waters (OG RS 35/96, 00/7). It was installed in 2004 by Limnos, Company for Applied Ecology. The new system consists of three beds. Both bed A and bed B are 5 m long and 4 m wide while the dimensions of the bed C are 5 × 8 m, in total 80 m^2. Figure 1 shows the scheme of the system and its longitudinal cross-section.

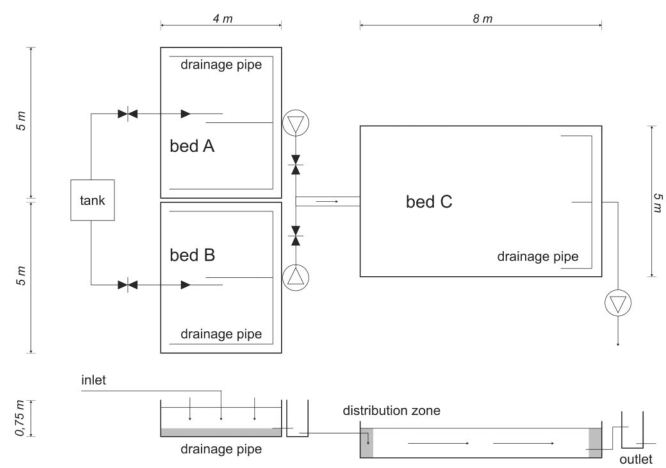

Figure 1: Constructed wetland.

The bottom of all beds was fortified with a 2 mm thick HDPE foil placed to ensure impermeability. The water level was regulated with the valve at the outlets of the beds. Beds were planted with *Phragmites australis* with five clumps m^{-2}, transferred from an old pilot plant. The actual retention time, measured by the electric conductivity was 40 hours by the hydraulic flow 1 l/min. The out flow was in the nearby stream.

Media consisted of gravel and sand and was composed as follows: bed A and B: fine sand, grain size 1-4 mm and sand, grain size 4-8 mm (1:1); bed C: fine sand, grain size 1-4 mm, 8-16 mm and gravel, grain size 32-64 mm (2.5 : 2.5 : 1).

Four analyses were made during the initial months of operation. Performance efficiency of the CW was evaluated from spring 2005 till autumn 2005 through selected physical and chemical parameters. Cumulative samples were taken monthly at three sampling points for analyses of COD, BOD_5, SAC, TOC, AOX, Cl^-, NH_4^+, NO_3^-, NO_2^- and total P. Sampling was carried out at the outflow into the vertical as well as into horizontal CW and at the outlet sump. Sampling was carried out according to the actual retention time. Analyses were performed by the independent laboratory according to standard methods (Faculty of Mechanical Engineering, University of Maribor, Slovenija; Faculty of Textile Technology, University of Zagreb, Croatia).

Preliminary Investigations

Determining optimal combination of easily accessible adsorbents, with an accentuation on their natural origin was the primary goal of preliminary investigations.

Laboratory model was designed as a vertical column, 19 cm high, 14 cm in diameter and 3967.39 cm^3 volume, with an outlet valve at the bottom of the column. Columns have been filled with various biological materials, which have purifying properties, were also investigated. These materials were: fine sand (grain size 0.5-1 mm), sand (grain size 1-4 mm), gravel (grain size 8-16 mm) and coarse gravel (grain size 32-64 mm) of varying mass ratio. Geo textile filter, PP (surface mass 500 g/m^2, thickness (20 N) 3.70 mm), has been used as a last filter component, placed at the bottom of the column (Figure 2). Purpose of this last component was to avoid burdening and clogging water pumps with small particles, which may occur in full scale pilot project purifying.

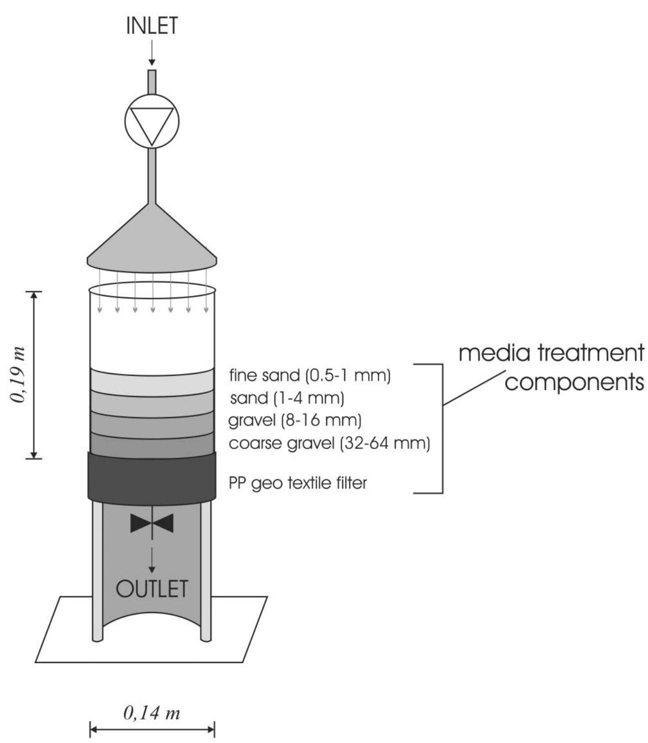

Figure 2: Simulated wetland.

Purified waste water was a mixture of two types of dye-house waste water received after dyeing with C.I. Reactive Black 5 (Figure 3) and C.I. Vat Red 13 (Figure 4).

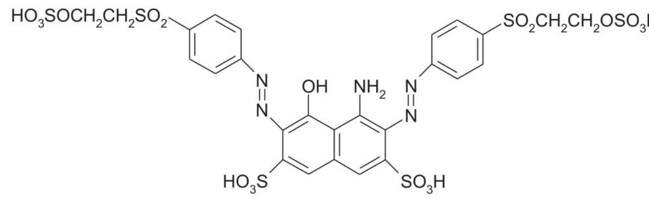

Figure 3: C.I. reactive black 5.

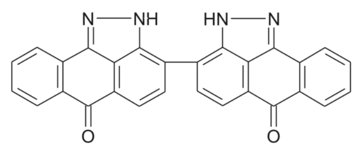

Figure 4: C.I. vat red 13.

Waste water, obtained after reactive and vat dyeing, also contained auxiliaries such as electrolyte, alkali, reduction expedient, surfactants, sequestrates etc.

Performance of purifying method has been evaluated by investigation of the following parameters:

1. pH
2. Electrical conductivity
3. Degree of decolouration
4. Chemical Oxygen Demand (COD), ISO 5220 B
5. Biochemical Oxygen Demand (BOD_5), EN 1899-2
6. Total Organic Carbon (TOC), ISO 5310
7. Special Absorbance Coefficient (SAC), ISO 7887
8. Absorbable Organic Halogens (AOX), EN 17025
9. Cl^- acc. Mohr

Results and Discussion

Considering the complexity of removing dyes used in textile industry from wastewater effluents, constructed wetlands are rarely used as a primary method of purifying. Possibility of removing dyes is primarily independent of their chemical constitution as well as concentration.

In this paper emphasis was given on biological purifying methods based on adsorptive properties of purifying system. Therefore, the main goal was to elaborate possibility of removing dyes using constructed wetland, without pretreating wastewaters either using physical or chemical methods e.g. Fenton reagent or poly electrolytes.

Full scale constructed wetland pilot project, described in the paper, is the first scientific approach to resolving dye-house wastewaters problem in the region. Secondary goal of the project was to educate people in the areas where water isn't recycled within a closed water cycle.

Results of Preliminary Investigations

Dye-house waste water has been analyzed in order of purifying process optimizing. Results of preliminary investigations referring to dye-house waste water to be purified are shown in Table 1.

Table 1: Dye-house waste water characterization

Parameters	*Values*
pH	7.5
Electrical conductivity (mS/cm)	22.5
SAC (436 nm, 525 nm, 620 nm)	40/98/70
COD (mg/l O_2)	2200
BOD_5 (mg/l O_2)	300
TOC (mg/l C)	500
AOX (mg/l)	1280
Cl^- (mg/l)	424

Preliminary investigations were, also, to determine the influence of fine sand on purifying effect. Past experience based on constructed wetlands used for purifying waste waters of different origins, showed how fine sand of very low granulations can and will damage water pumps and cause excess water pressure (Bulc and Sajn-Slak, 2003; Sajn-Slak et al., 2005; Parac-Osterman et al., 2004; Ojstrsek and Golob, 2004). Table 2 shows how obtained measured values vary depending on column mass ratio and how presence of fine sand didn't significantly improve the effect.

Table 2: Characterization of purified dye-house waste water

Media building components		*Column*		
		1	*2*	*3*
Mass ratio	fine sand	3	2.5	0
	sand	1	2.5	2.5
	gravel	2	2.5	2.5
	coarse gravel	2	1	1
Parameters				
pH		7.1	7.2	6.9
Electrical conductivity (mS/cm)		10.5	8.2	7.5
AOX (mg/l)		82	65	70
COD (mg/l O_2)		300	200	150
BOD_5 (mg/l O_2)		150	100	100
TOC (mg/l C)		100	50	45
Cl^- (mg/l)		60	75	84
SAC	436 nm	2	6	15
	525 nm	10	12	20
	620 nm	8	10	15

Results of CW Purifying

Phragmites Australis plants have been planted in April and were given three months of growth time, while all measurements were performed in July. During the measurements there has been no rainfall and temperature ranged from 25 to 30 °C.

Waste water entering the purifying process has been characterized through a vast number of parameters. Measured values (Table 3) are typical for waste waters obtained after dyeing. Additional investigations were made in order of describing what would roughly be called a nitrogen cycle, which is along with the total amount of phosphorus a very important link in a unified eco-cycle of CW. Low values of ammonium, nitrate and nitrite suggest that waste water was obtained by mixing dye-house waste water with fecal waste waters, amount of which was low according to measured values.

Table 3: Industrial dye-house waste water characterization (INLET)

Parameters	*Values*
pH	7.16
Electrical conductivity (mS/cm)	2.42
SAC (436 nm, 525 nm, 620 nm)	34/100/5
COD (mg/l O_2)	1379
BOD_5 (mg/l O_2)	320
TOC (mg/l C)	425
AOX (mg/l)	1080
Cl^- (mg/l)	512
NH_4^+ (mg/l)	2.15
NO_3^- (mg/l)	0.11
NO_2^- (mg/l)	0.17
Total P (mg/l)	4.32

As it can be seen in results shown below, water flow has been taken as the most important variable of the purifying process. Logically, the most efficient purifying efficiency was to be obtained at lowest water flow of 1 l/min. Shown results refer to measurements obtained for column 3 (Table 2). Columns 1 and 2 (Table 2) did not exhibit satisfactory results, whilst causing excess water pressure and pump clogging, after long term purifying.

Figure 5 exhibits results obtained after purifying. Water flow of only 1 l/m gave the most efficient results (reduction efficiency of over 90% for all parameters

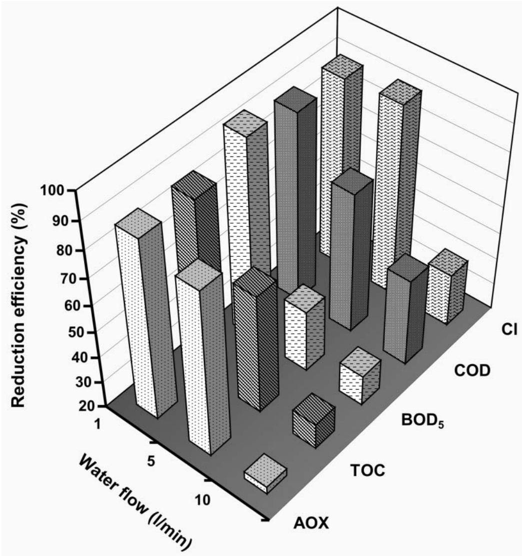

Figure 5: Characterization of purified Textina dye-house waste water (Outlet).

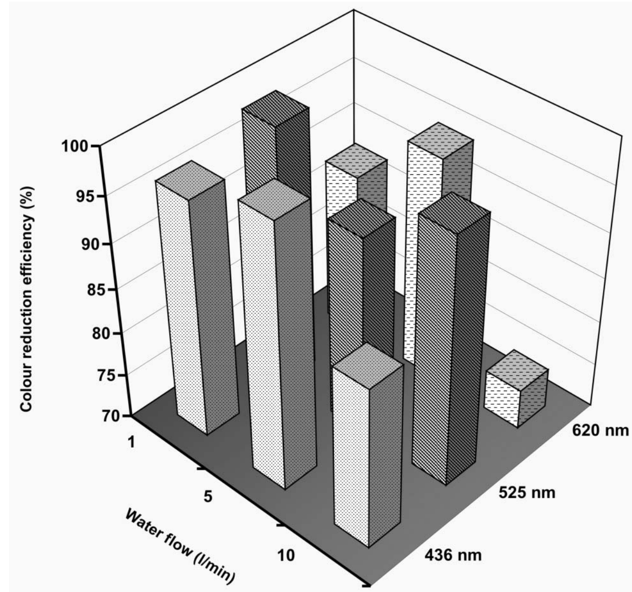

Figure 6: CW colour reduction efficiency for Textina dye-house waste water (Outlet).

measured). However, increase of water flow to up to 5 l/min did not significantly reduce system's efficiency (parameters were within legally permitted). Further increase of water flow would additionally improve cost benefit of the system presented, but it gave unsatisfactory results concerning maximum allowed values. Parameter BOD_5 was most influenced by the increase in water flow.

Colour reduction efficiency was measured through calculation of SAC (special absorption coefficient) values (measured at wave lengths of 436, 525 and 620 nm). Results show (Figure 6) how colour reduction efficiency significantly decreases with the increase in water flow, exhibiting lowest SAC value at water flow of 10 l/min and wave length of 620 nm.

pH levels have been measured throughout the whole purifying process and didn't exhibit major fluctuations (around 7.3).

Adsorption of dyestuff on natural adsorbents was reciprocal to time, which was in accordance with system's dynamics. This was expected and can be best seen in Figures 5 and 6. Therefore, further analysis of nitrogen and phosphorus compounds was carried out for 5 l/min water flow.

Amount of nitrates and nitrites (Figure 7) when compared to entry values has decreased. However, amount of ammonium showed significant increase, which was probably the result of nitrifying bacteria absence. Unexpected high amount of ammonium obtained for water flow of 5 l/min was the result of the CW

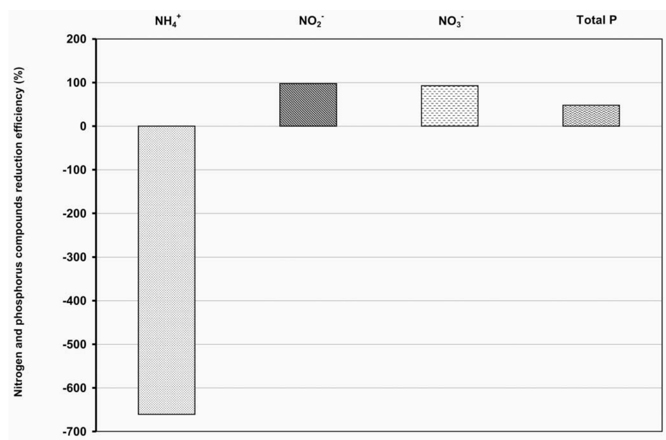

Figure 7: CW nitrogen and phosphorus compounds reduction efficiency for Textina dye-house waste water (Outlet) (water flow of 5 l/min)

heterogeneity. Partial increase of fecal waters within the amount of total waste waters purified would cause more successful decomposition of ammonium to nitrites and nitrates, which are then used through enzymes and plants for the production of amino acids and nucleic acids. Most of the phosphates in textile industry end up in waste waters through use of detergents, while discharge of untreated and treated municipal sewage and industry waste water can all add excess phosphate to near-by waters. Then, an excess growth off algae, called an algal bloom, may occur (Figure 6).

Conclusion

Construction of wetland was preceded by preliminary investigations, an imperative step of the project, used in order to predict the behaviour of full scale model. Best results of preliminary investigations were obtained by assembling treatment media adsorbents accordingly to real geological profiles. Although, using adsorbents of lower granulation (columns 1 and 2) exhibited better results considering removal of dyes, low granulation sand caused, either burdening or even clogging water pumps. It was because of this phenomena, column 3 (Table 2) combined with *Phragmites Australis* had to be used when pilot project was built. All of the afore-mentioned confirms the problem of dye removal suggesting a need of preceding chemical and physico-chemical methods in order of removing completely all of the dyestuff from wastewater effluents.

Results proved that variable influent as well as the hydraulic load has great influence on the system's efficiency (for all measured parameters: COD, BOD_5, SAC, TOC, AOX, Cl^-, NH_4^+, NO_3^-, NO_2^-, total P). Although, greater efficiency was obtained with lesser hydraulic load it exhibited poor cost benefit, which led to the conclusion how hydraulic load of 5 l/min was optimal, regarding purifying efficiency vs. cost benefit.

Because the use of CW did not lead to complete decolouration (cca. 8% of dyestuff resides in waste water), additional purifying through biological filter (optimized within E!2983 Project) had to be carried out in order to obtain the limits regulated through legislation.

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