UNIVERSITY OF NOVA GORICA
GRADUATE SCHOOL

Lucija Kobal

Advanced technologies for colour removal and technological water reuse of textile effluent

Master thesis

Mentors: prof. dr. Sidney Katz, dr. Polonca Trebše Asst. Prof

Nova Gorica, 2007

ACKNOWLEDGMENTS

The success of this work is due to the commitment and goodwill of many people.

First of all, I would like express my deepest sense of gratitude to my mentor dr. Polonca Trebše Asst. Prof. for her patient guidance, encouragement and excellent advice throughout my thesis.

My sincere thanks to my co-mentor Prof. dr. Sidney Katz for his comments and suggestions for editing of my thesis.

I am thankful to company Tekstina d.d. for financial and valuable support with wastewater during the research.

Finally, I take this opportunity to thank my parents and friends for their moral support and patience during my study.

SUMMARY

Textile industries consume substantial volumes of water and chemicals for wet processing of textile. These chemicals are used for desizing, scouring, bleaching, dying, printing and finishing. The continued increase in the costs, of chemicals, energy and water make recovery more important today then it was years ago. Advanced technologies are increasingly being considered as an alternative to conventional wastewater treatment methods in anticipation of further demands for cleaner technology and water reuse in textile industry.

Three different advanced technologies were evaluated in the pilot scale (revere osmosis pilot plant, constructed wetland pilot plant and hydrogen peroxide pilot plant) using “real process wastewater” originating from finishing processes of company Tekstina d.d.
The results gained with pilot plant study of a wastewater from textile company show promising results and will be used for a possible application of investigated technologies to textile plant Tekstina d.d. concerning cleaner technology (energy consumption and water reuse). Results of pilot study are only guidelines for further work because they can only relate to specific points in time and small samples.

POVZETEK

Tekstilna industrija porablja precejšnje količine vode in kemikalij za mokro obdelavo tkanin. Te kemikalije se uporabljajo za škrobljenje, pranje, beljenje, barvanje, tiskanje in oplemenitenje. Nadaljnje naraščanje stroškov kemikalij, energije in vode daje v današnjem času večjo pomembnost ponovni uporabi vode kot je bilo nekoč. Napredne tehnologije čiščenja postajajo vedno bolj pomembne kot alternativa konvencionalnim metodam čiščenja odpadnih vod za izpolnjevanje nadaljnjih potreb po čistih tehnologijah in ponovni uporabi vode v tekstilni industriji.

Na pilotni ravni so se primerjale tri različne napredne tehnologije, (pilotna naprava za reverzno osmozo, pilotna naprava za rastlinsko čistilno napravo in vodikov peroksid/UV pilotna naprava) z uporabo »prave procesne vode« pripeljane iz procesa oplemenitenja podjetja Tekstina d.d.. Pridobljeni rezultati s študijo pilotnih naprav z vodo iz tekstilnega podjetja kažejo obetajoče rezultate in se bodo uporabili za morebitno aplikacijo preiskovanih tehnologij v tekstilno podjetje Tekstina d.d.. Rezultati pilotne študije so samo smernice za nadaljnje delo, saj se nanašajo na določne meritve, čase in majhne vzorce.

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SYMBOLS, ABBREVIATIONS

Table A: List of symbols

Symbol	**Explanation**
L	Litre
Kg	Kilogram
%	Percent sign
L kg^{-1}	Litre per kilogram
m^3kg^{-1}	Cubic meter per kilogram
mg L^-	Milligram per litre
Hv	*h* = Planck's constant (in J·s) *v* = Frequency (in Hz)
Lmh	Litre per square meter of membrane per hour
P	Pressure
Bar	Unit of pressure
µm	Micrometer (unit of length)
V	Volt
Nm	Nanometre
m^3/day	Cubic meter per day
g/mol	Gram per mol
mg/L	Milligram per litre
°C	Degrees celsius
N	Nitrogen
P	Phosphorus
Cu	Cupper
Cd	Cadmium
Cr	Chromium
Pb	Lead
Al	Aluminium
Zn	Zinc
Co	Cobalt
Sn	Tin
Cr	Chromium
Fe	Iron
NaOH	Sodium hydroxide
H_2O_2	Hydrogen peroxide
O_3	Molecular formula for ozone
CO_2	Carbon dioxide
H_2O	Water
$OH^•$	Hydroxyl radical
Cl^-	Chloride ion
NaOCl	Sodium hypochlorite
–N = N–	Azo group
–C = C –	Carbon-carbon bond is a covalent bond
H_2SO_4	Sulfuric acid
- SO_4	Sulphate
- SO_3	Sulphite
-S	Sulphide
m^3/y	Cubic metre per year
$N0_3$-N	Nitrate-nitrogen
$N0_2$-N	Nitrite- nitrogen
Hg	Mercury
W	Watt
m^3/h	Cubic metre per hour
mg/l	Milligram per litre
l/min	Litre per minute
NH_3-N	Ammonia Nitrogen

Table B: List of abbreviations

Abbreviation	**Explanation**
pH	Is a measure of the acidity or basicity of a solution
COD	Chemical oxygen demand
BOD	Biological oxygen demand
UV	Ultraviolet
EU	European Union
EPA	Environmental Protection Agency
AOX	Adsorbable Organic Halogens
TSS	Total suspended solids
ppm	Parts per million
EDTA	Ethylenediaminetetraacetic acid
€	Euro (currency sign)
SSF	Solid-state fermentation
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse osmosis
AOP	Advanced oxidation process
PVA	Polyvinyl alcohol
CW	Constructed wetland
TOC	Total Organic Carbon
LKCH	Lahko hlapni halogenirani ogljikovodiki
EO	Ekološka obremenitev (ecological charge)
SAC	Special Absorbance Coefficient
WTP	Wastewater treatment plant
AOX	Absorbance Organic Halogen
SIST	Slovenski inštitut za standardizacijo
ISO	International Standards Organization
DIN	Deutsches Institut für Normung
EN	European Norm
P_{UV}	Power of Ultraviolet lamp

1. INTRODUCTION

Textile industries produce large amounts of wastewater due to high consumption of water primarily in the dyeing and finishing operations. Typically 200-400 L of water is needed to produce 1 kg of product. The source of the polluting compounds when the cotton is utilized are the natural impurities extracted from the fibre, the processing chemicals and dyes.
Textile wastewater is a significant pollution source containing high concentration of inorganic and organic chemicals and is highly coloured from the residual dyestuffs. Thus generated effluents contain a wide range of contaminants, such us salts, dyes, surfactants, oil and grease, oxidizing and reducing agents. In environmental terms, those contaminants mean suspended solids, COD, BOD, as well high pH and very strong colour.
Colour is the first contaminant to be recognized in wastewater and has to be removed before discharging into water bodies or on land. The presence of very small amounts of dyes in water (less then 1ppm for some dyes) is highly visible and affects the water transparency and gas solubility in lakes, rivers and other water bodies (Robinson, et.al. 2001 and Bianchi et. al. 1999).

In the past, textile waste water has been usually treated in an activated sludge plant to allow wastewater discharge within low requirements but not in order to produce final effluent suitable for reuse in the textile process. Increasing water consumption for industrial and domestic processes in many European countries also force to increase water costs for wastewater treatment. Water reuse management has become an important operational and environmental issue. Wastewater reclamation and reuse are effective tools for sustainable industrial development programs. The treatment costs of wastewater and disposal have increased the economic incentive for implementing water reuse and water recycle process in industry. Increasingly stringent environmental legislation and generally enhanced intensity, efficiency, and diversity of treatment technologies have made the reuse of water more viable in many industrial processes (Dverioniene, et.al., 2003).

The purpose of this work is to compare three different technologies to reduce and recycle pollution load at the source where the pollution is generated within the textile plant. In my work I have chosen three different not conventional treatment technologies and each belong to different technology;

- filtration (reverse osmosis pilot plant)
- remediation (wetland pilot plant)
- advance oxidation technology (hydrogen peroxide/ UV pilot plant)

2. OBJECTIVES

The aim of experiments was to investigate three advanced technologies in the pilot scale using "real process wastewater" originating from finishing processes of company Tekstina d.d. Therefore, the objectives of these pilot experiments were:

- to present the quality of textile wastewater in the company Tekstina with respect to water consumption and water costs
- to reduce decolouration of textile wastewater
- to investigate advantages and disadvantages of each technology
- to investigate the most appropriate available technologies and possible application of one or more of these technologies to textile plant Tekstina d.d
- to evaluate an economical solution to improve water quality and reduce water costs for the company Tekstina d.d.

3. THEORY

3. 1. Textile and clothing industry in Europe

The following section is based on data collected by the Enterprise Directorate of the European Commission and reported by Stengg (2001).
The textile and clothing industry represents an important source of income and employment for many countries. In 1999, it corresponded to 5.7% of the production value of world manufacturing output, and more than 14% of world employment.
Europe's contribution in textiles production was 29% in 1998, similar to that of the Americas, but lower than the Asian one (39%). The European textile and clothing industry is characterised by a large number of small and medium-sized enterprises: in the year 1999, 120,000 companies employed more than 2 million people (average 19 employees per company) and created a turnover of € 178 billions.
The relative weight in the overall EU manufacturing industry was about 4% of total production and 7.6% of employment. Within the total EU textile and clothing activities, based on a combination of economic indicators as 'turnover', 'value added', and 'employment', (Stengg, 2001) clothing accounts for about 40% and textiles for the remaining 60% (12% of it being covered by finishing activities). Italy is by far the most important country in Europe (31% of the EU total), followed by the United Kingdom (15%), Germany (14%), France (13%), Spain (9%), and Portugal (6%). European industries process all kind of fibres, the great part are today man-made fibres (72% in 1998 in terms of volume) while among natural fibres cotton is by far the most important.

3. 2. Characteristics of textile water and wastewater

The textile industry is a large user of water. The average water consumption in textile processes is 200-400L to produce 1kg of finished product (Marcucci, 2001). Because it is a chemically intensive industry, textile finishing generates effluents containing significant amounts of a wide range of residues.

3. 3. Supply water

Both water consumption rates and supply water characteristics are highly variable. The highest water use generally refers to natural fibres, and particularly to cotton. Synthetic fibres require lower water volumes per unit of product, mainly due to the lower cleaning and scouring needs. Almost the entire volume of the water used is eventually discharged because losses (by steam production and evaporation from hot baths during the dyeing and drying operations) are low. On average, the effluents volume corresponds to 90–95% of the water used.

Some data of water used per unit weight of processed fibre are reported in Table 1 (EPA, 1996) and Table 2 (Antonelli & Rozzi, 2001).

Table 1 *Average, minimum and maximum water supply for different textile operations (EPA, 1996).*

Subcategory			Water Usage (L kg^{-1})		
			Min	Med	Max
1		Wool scouring	4.2	11.7	77.6
2		Wool finishing	110.9	283.6	657.2
3		Low water use processing	0.8	9.2	140.1
4		Woven fabric finishing			
	a	Simple processing	12.5	78.4	275.2
	b	Complex processing	10.8	86.7	276.9
	c	Complex processing plus desizing	5.0	113.4	507.9
5		Knit fabric finishing			
	a	Simple processing	8.3	135.9	392.8
	b	Complex processing	20.0	83.4	377.8
	c	Hosiery processing	5.6	69.2	289.4
6		Carpet finishing	8.3	46.7	162.6
7		Stock and yarn finishing	3.3	100.1	557.1
8		Non-woven finishing	2.5	40.0	82.6
9		Felted fabric finishing	33.4	212.7	930.7

Table 2 *Water supply per unit weight of processed fibre in Como textile area (Italy) (Antonelli & Rozzi, 2001).*

Fibre type	Water supply (m^3 kg^{-1})
Yarn Dye-works	
Polyester	0.051
Silk	0.082
Viscose	0.082
Fabric Dye-works	
Polyester	0.090
Printing and Finishing	
Polyester	0.320
Silk	0.183
Cotton–viscose	0.458
Wool	0.275

3. 4. Textile wastewater

Wastewater is by far the largest waste stream of the textile industry. It includes: cleaning water, process water, non contact cooling water and storm water (EPA, 1997). The amount of water used varies widely, depending on the specific process operated at the mill, the equipment used and the prevailing management approach regarding water use. For example, in the Como textile area, most dyers are traditionally hostile to water reduction policies assuming that high quality of the products is assured only by using high water volumes.
Scouring, dyeing, printing and finishing generate the majority of textile wastewater, as they require many rinsing sequences after each step. As an average, 60 to 90% of the total water consumption is for rinsing purposes (Groves et al., 1979).

Because of the wide variety of process steps, textile wastewater typically contains a complex mixture of organic and inorganic chemicals. Table 3 presents a summary of compounds potentially released during the various textile operations.

Table 3 *Potential specific pollutants from textile wet processing operations (Adapted from EPA, 1997 and Correia et al., 1994).*

Process	**Compounds**
Desizing	Sizes, enzymes, starch, waxes, ammonia
Scouring	Disinfectants and insecticides residues, NaOH, surfactants, soaps, fats, waxes, pectin, oils, sizes, anti-static agents, spent solvents, enzymes
Bleaching	H_2O_2, AOX, sodium silicate or organic stabiliser, high pH
Mercerising	High pH, NaOH
Dyeing	Colour, metals, salts, surfactants, organic processing assistants, sulphide, acidity/alkalinity, formaldehyde
Printing	Urea, solvents, colour, metals,
Finishing	Resins, waxes, chlorinated compounds, acetate, stearate, spent solvents, softeners

Desizing in some cases combined with scouring, is one of the industry's largest sources of wastewater pollutants (EPA, 1997), contributing to a relevant part of the total organic pollution in wastewater (Snowden-Swan, 1995). The specific polluting load of sizing agents is 1 - 2 grams of COD per gram of size. Natural sizes, such as those based on starch or proteins, are also characterised by a high BOD and a BOD/COD ratio of 0.6 – 0.7. Synthetic size agents such as polyvinyl alcohol or carboxymethyl cellulose, on the contrary, have an almost null BOD. The organic load due to desizing can be roughly calculated on the basis of the amount of size applied in the previous phases (the size applied is usually 5 to 20 % on a weight basis of the yarn treated).
The pollutants content of scouring effluents depends on the nature and quantity of the impurities present on the fibres and on the intensity of the process itself. High TSS and high organic loads are common in effluents from natural fibres scouring, due to the removal of dirt, waxes, vegetable matter, etc. Soaps, detergents, alkali, solvents, as well as pesticides may also be present (Table 3).
Synthetic fibres usually require milder scouring operations, to remove sizes or oils previously applied. For these fibres, scouring and desizing are frequently combined in a single process.
In the bleaching step the most common agents are: hydrogen peroxide, sodium hypochlorite, sodium chlorite and sulphur dioxide gas. Hydrogen peroxide is by far the most commonly used bleaching agent for cotton and cotton blends, covering over 90 % of the bleach used in textile operations (EPA, 1997) and it is typically dosed in caustic solutions.
Mercerising is used for cotton to enhance the following dye application and the lustre of fibres. It is carried out with solutions of caustic soda followed by neutralisation and several rinses. Alkali consumption may be about 20 % of the weight of goods (EPA, 1997).
The nature of textile wastewater, in terms of broad parameters such as BOD, COD, TSS, N, P, has extensively been reviewed by different authors (Jekel et al., 1997, Correia et al., 1994, EPA 1996) and in Table 4 average concentration and specific loads for main operations are reported (Correia et al., 1994).

Table 4 *Average concentration and specific loads for main operations in textile finishing*

Fibre	***Process***	***pH***	***BOD(mg L^{-1})***	**TSS(mg L^{-1})**
Cotton	Desizing		1,700-5,200	16,000-32,000
	Scouring or Kiering	10-13	50-2,900	7,600-17,000
	Bleaching	8.5-9.6	0-1,700	2,300-14,000
	Mercerising	5.5-9.5	45-65	600-1,900
	Dyeing	5-10	11-1,800	500-14,000
	Scouring	9-14	30,000–40,000	1,100-64,000
Wool	Dyeing	4.8-8	380-2,200	3,900-8,300
	Washing	7.3-10.3	4,000-11,000	4,800-19,000
	Neutralisation	1.9-9	28	1,200-4,800
	Bleaching	6	390	900
Nylon	Scouring	10.4	1,400	1,900
	Dyeing	8.4	370	640
Acrylic/ Modacrylic	Scouring	9.7	2,200	1,900
	Dyeing	1.5-3.7	170-2,000	830-2000
	Final scour	7.1	670	1,200
Polyester	Scouring		500-800	
	Dyeing		480-27,000	
	Final scour		650	
Viscose	Scouring and dyeing	8.5	2,800	3,300
	Salt bath	6.8	58	4,900
Acetate	Scouring and dyeing	9.3	2,000	1,800

In the view of pollution prevention and reduction, the pollutants of major concern are recalcitrant or hazardous organics, such as dyes or some surfactants, metals and salts. They will be briefly discussed in the following sections.

3. 4. 1. Dyes

In the past, highly coloured waste streams were considered objectionable primarily for aesthetic reasons. More recently, the main concern is associated with the recalcitrance and potential toxicity of xenobiotic compounds (Tan, 2001). Even though some dyes considered potentially toxic have been withdrawn from the market and new, more biodegradable molecules have recently been developed, textile dyes are still a major source of water pollution. Of the 700,000 tons of dyes annually produced world-wide, about 10 to 15 % is disposed of in effluents from dyeing operations (Snowden-Swan, 1995).
Two different approaches are used to classify dyes, the first one is based on the nature of the chromophore (the aromatic group absorbing visible light to impart colour) while the second follows the mode of application. According to the first criteria, twelve dye classes are usually defined among which the most important group are azo dyes, because of the great extent in number and tonnage of their application (Carliell et al., 1998). Azo dyes can be used on natural fibres (cotton, silk, wool) and synthetic fibres (polyesters, polyacrylic, rayon, etc.); their molecules include one or more azo groups (–N=N–). The second classification of dyes includes seven classes: acid, basic, direct, disperse, reactive, sulphur and vat. (Table 5) Details on their characteristics, typical uses and degree of fixation can be found in EPA (1997) and Jekel (1997).

Table 5 *Typical Characteristics of Dyes Used in Textile Dyeing Operations*

Dye Class	Description	Method	Fibres Typically Applied to	Typical Fixation (%)
Acid	water-anionic compounds	Exhaust / Beck / Continuous (carpet)	wool, nylon	80-93
Basic	water-soluble, applied in weakly acidic dye baths; very bright dyes	Exhaust / Beck	acrylic, some polyesters	97-98
Direct	water soluble, anionic compounds; can be applied directly to celluloses without mordents (or metals like chromium or copper)	Exhaust / Beck Continuous /	cotton, rayon, other celluloses	70-95
Disperse	not water-soluble	High temperature exhaust, Continuous	polyester, acetate, other synthetics	80-92
Reactive	water-soluble, anionic compounds; largest dye class	Exhaust / Beck, Cold pad batch Continuous	cotton, other celluloses, wool	60-90
Sulphur	organic compounds containing sulphur or sodium sulphide	Continuous	cotton, other celluloses	60-70
Vat	oldest dyes; more chemically complex; water-insoluble	Exhaust / Package/ Continuous	cotton, other celluloses	80-95

Overlaps of the two classifications are possible e.g. azo dyes may belong to the acid, direct, disperse, basic, reactive and vat dye classes. Significant differences in the degree of fixation are reported for the various dye classes. Reactive dyes, which nowadays make 20 – 30 % of the total dyes market (Vandevivere et al., 1998), are characterised by a low fixation rate, particularly the mono-reactive dyes (Wenzel et al., 1997), that represents the major concern about this dye class. It is obvious that the lower the fixation, the higher the residual colour and COD discharged in dyeing and rinsing operations. After reactive dyeing operations, as much as 800 mg L^{-1} of hydrolysed reactive dye may remain in the bath water (Steenken–Richter & Kermer, 1992).
Dyes are always used in combination with other chemicals (acids, alkali, salts, fixing agents, carriers, dispersing agents, surfactants, etc.) that are partly or almost completely discharged in the effluents together with the numerous additives and impurities present in the commercial dye products.

3. 4. 2. Metals

The concentration of heavy metals in textile mills has decreased in the last decade, mainly because of the reduction of metals contents in the dyes. Metals include copper, cadmium, chromium, nickel, lead and zinc. Sources of metals in the effluents may be fibres, supply water, dyes and chemical impurities. Dyes may contain metals such as zinc, nickel, chromium and cobalt, as functional part of the dye molecule or as impurities (EPA, 1997). Heavy metals concentrations in dyebath effluents, typically in the range of 1 to 10 mg L^{-1}, were reviewed by Correia et al., (1994).

3. 4. 3. Recalcitrant and hazardous organics

The biodegradability of textile wastewater has been increasing during recent years, thanks to substitutions of the chemicals used in the process (Vandevivere et al., 1998). In addition to the dye molecules, mostly non biodegradable in aerobic conditions, the persistent organics include: surfactants or their by-products, dyeing auxiliaries such as polyacrylates, phosphonates, sequestering agents (EDTA), synthetic sizes, anti-static, dispersing or fixing agents, preservatives and a large number of finishing auxiliaries.
Hazardous organic wastes may also result from the use of solvents in some scouring or printing operations (EPA, 1997), while halogenated organic compounds (AOX) may derive from hypochlorite bleaching operations or from spent liquors following shrink-proofing finishing treatment by chlorine. AOX concentrations up to 100 mg L^{-1} have been reported by Steiner (1995) in bleaching effluents, including considerable amounts of carcinogenic chloroform. Nowadays, however, bleaching is mostly performed with hydrogen peroxide. Finally, it is worth noting that some reactive dyes are AOX.

3. 4. 4. Salts

The presence of salts have been identified as a potential problem in textile dyeing wastewater. Many salts are either used as raw materials or produced as by-products of neutralisation or other reactions in textile wet processes. Salt concentrations in effluent from cotton dyeing may reach 2,000 to 3,000 ppm and quantities of salts added in dyeing operations range from 20 to 80 % of the weight of the good (EPA, 1996).

3. 5. Method of decolouration

The colour of water, polluted with organic colorants, decreases when cleavage of the –C = C – bonds, the –N = N – bonds and heterocyclic and aromatic rings occurs. The absorption of light by the product of photochemical reaction shifts from the visible to the ultraviolet or infrared region of the electromagnetic spectrum (Strickland et.al.,1995).
There are several ways in which colorants cause problems in water (Slokar et. al.,1998): depending on exposure time and dye concentration, dyes can have acute and/or chronic effects on exposed organisms.
Although visibility of dyes in rivers depends on their colour, and extinction coefficient and on the clarity of the water, they are inherently highly visible. This means that even minor releases of effluents may cause abnormal colouration of surface waters which captures the attention of both the public and authorities.
Neglecting the aesthetic problems, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water. This interferes with the growth of bacteria to levels sufficient to biologically degrade impurities in the water and start the food chain.
The main methods of textile wastewater treatment are divided on three techniques (Slokar and Le Marechal et. al.,1997): chemical, physical and biological. Currently the main methods of textile dye treatment are by physical and chemical treatment. Advantages, disadvantages and comparison of these methods is given in table 6.

Table 6 *Advantages and disadvantages of the current methods of dye removal from industrial effluent:*

Chemical methods	**Advantages**	**Disadvantages**
Fenton reagents	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied gaseous state; no alteration of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by products
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are not hazardous	High cost of electricity
Physical methods	**Advantages**	**Disadvantages**
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Required a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production

3. 5. 1. Chemical methods

Oxidative process is the most commonly used method of decolourisation because of its simple handling. The main oxidising agent is usually hydrogen peroxide (H_2O_2), which needs to be activated. Decolouration methods differ in the way in which hydrogen peroxide is activated (Slokar and Le Marechal, et. al., 1997). Chemical oxidation removes the dye from the dye-containing effluent by oxidation resulting in cleavage of the aromatic rings in the dye molecules.

3. 5. 1. 1. H_2O_2 –Fe (II) salts (Fenton's reagent)

Fenton's reagent (hydrogen peroxide, activated with Fe(II) salts) is suitable for treating the wastewaters which are resistant to biological treatment or are poisonous to the biomass. Chemical separation uses the action of sorption or bonding to remove dissolved dyes from wastewater and has been shown to be effective in decolourising wastewater containing both soluble and insoluble dyes. Besides offering advantages in reduction of COD, colour and toxicity, this process also has main disadvantage, which is sludge generation through the flocculation of the reagent and the dye molecules. The sludge, which contains the concentrated impurities, still requires disposal. (Slokar and Le Marechal, et. al., 1997)

3. 5. 1. 2. H_2O_2 – ozone

The use of ozone for purposes of wastewater treatment began in the early 1970s (Strickland, et. al.,1995). Because of its instability ozone is a very powerful oxidising agent. Its oxidation potential is 2.07 V compared to chlorine, which is 1.36 V. The original purpose of oxidation with ozone is disinfection of potable water. One major advantages is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge. A disadvantage of ozone is its short half-life, typically being 20 min. This time can be further shortened if dyes are present. In addition, the stability of ozone is affected by the presence of salts, pH, and temperature. Under alkaline conditions ozone decomposes more rapidly then under acidic conditions.
In H_2O_2 –O_3 process ozone is used as hydrogen peroxide activator. Activator is needed for the formation of hydroxyl radicals, whose oxidation potentials are much higher then that of hydrogen peroxide. With this process there are many advantages; no sludge formation, no salt formation, short reaction times. The process also has disadvantages; not applicable for all dye types, toxicity, hazard, problematic handling, no COD reduction, additional load of water with ozone (Slokar and Le Marechal, et. al., 1997).

3. 5. 1. 3. H_2O_2 –UV radiation

This photochemical method degrades dye molecules to CO_2 and H_2O by UV treatment in the presence of H_2O_2 (Yang et. al., 1998). Degradation is caused by the production of high concentration of hydroxyl radicals. UV light my be used to activate chemicals, such us H_2O_2, and the rate of dye removal is influenced by the intensity of UV radiation, pH, dye structure and the dye bath composition (Slokar and Le Marechal, et. al., 1997). Depending on initial materials and the extent of decolourisation treatment, additional by-products, such us halides, metals, inorganic acids, my be produced (Yang et. al., 1998). There are advantages of this treatment of dye containing effluent; no sludge is produced and foul odours are greatly reduced. UV light activates the destruction of H_2O_2 into two hydroxyl radicals and this causes the chemical oxidation of organic materials.

$H_2O_2 + h\nu \rightarrow 2OH^{\bullet}$

3. 5. 1. 4. Sodium hypochloride (NaOCl)

Chemical oxidation of coloured wastewater is also possible with sodium hypochlorite. This method attacks at the amino groups of the dye molecule by the Cl^-. It initiates and accelerates azo-bond cleavage. This method is unsuitable for dispersed dyes (Namboodri, et.al.,1996). An increase in decolouration is seen with an increase in sodium hypochlorite concentration. The use of sodium hypochlorite for dye removal is becoming less frequent due to negative effects it has when released into waterways and the release of aromatic amines which are carcinogenic, or otherwise toxic molecules (Slokar and Le Marechal, et. al., 1997).

3. 5. 1. 5. Cucurbituril

Cucurbituril was first mentioned by Behrand et. al. (1905), and then rediscovered in the 1980s by Freeman et.al 1981. This is a promising new sorbent for removal of reactive dyes by sorption in the cage compound cucurbituril. Cucurbituril is a cyclic polymer of glycoluril and formaldehyde. Its structure reminds one of a pumpkin, which belongs to the botanical family of cucurbituaceae. The uril, indicates that a urea monomer is also part of this compound. To be industrially feasible, cucurbituril would need to be incorporated into fixed bed sorption filters. Like many other chemical methods, cost is major disadvantages (Karcher et. al., 1999b).

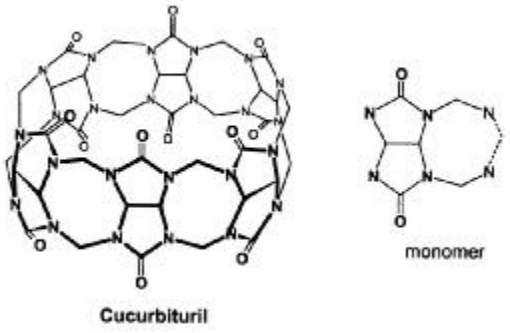

Figure 1: *Structure of cucurbituril and its monomer*

3. 5. 1. 6. Electrochemical destruction

This is relatively new technique, which was developed in the mid 1990s. It has some significant advantages for use as an effective method for dye removal. There is little or no consumption of chemicals and no sludge build up. The break down products are generally not hazardous permitting the release of treated wastewaters back into water ways. It shows efficient and economical removal of dyes and a high efficiency for colour removal and degradation of recalcitrant pollutants. Relatively high flow rates cause a direct decrease in dye removal, and the cost of electricity used is comparable to the price of chemicals (Robinson et.al., 2001).

3. 5. 2. Physical methods

Adsorption techniques have gained favour recently due to their efficiency in the removal of pollutants too stable for conventional methods. Adsorption produces high quality product, and is a process which is economically feasible. Decolouration can be achieved by two mechanisms: adsorption and ion exchange (Slokar and Le Marechal, et. al., 1997), and is influenced by many physic-chemical factors, such as, dye/sorbent, interaction, sorbent surface area, particle size, temperature, pH and contact time (Robinson , et.al., 2001).

3. 5. 2. 1. Activated carbon

Activated carbon is the most commonly used material for dye removal by adsorption and is very effective for adsorbing cationic, mordant, and acid dyes and to a slightly less extent, dispersed, direct, vat, pigment and reactive dyes (Nasser and EL-Guendi et. al., 1991). Performance is dependent on the type of carbon used and the characteristics of the wastewater. Activated carbon, like many other dye-removal treatments, can be well suited for one particular waste system and ineffective in other. Activated carbon is expensive. The carbon also has to be reactivated otherwise disposal of the concentrates has to be considered. Reactivation results in 10-15% loss of the sorbent.

3. 5. 2. 2. Peat

Peat has the ability to adsorb transition metals and polar organic compounds from dye-containing effluents. Peat my be seen as a viable adsorbent in countries such as Ireland and UK, where it is widely available. Peat requires no activation, unlike activated carbon and also cost much less (Poots and McKay, et.al.,1976). Spent peat may be burned and utilised for steam production. Due to activated carbon's powder nature, it has a much larger surface area and hence has a better capacity for adsorption.

3. 5. 2. 3. Wood chips

Chipped wood shows a good adsorption capacity for acid dyes although due to its hardness, is not as good as other available sorbents and longer contact times are required (Nigam et. al., 2000). After being used to adsorb the dye, the spent material can be burned to generate power although there is potential for solid-state fermentation (SSF) of dye adsorbed wood chips.

3. 5. 2. 4. Fly ash and coal (mixture)

A high fly ash concentration increases the adsorption rates of the mixture due to increasing the surface area available for adsorption. This combination my be substituted for activated carbon, with a ratio of fly ash: coal, 1: 1 (Gupta et.al., 1990).

3. 5. 2. 5. Other materials

Natural adsorbents such as natural clay, rice hulls, maize cob have also been studied and found effective and cheaper when compared with activated charcoal(Nigam et.al.,2000). These materials are so cheap regeneration is not necessary and the potential exists for dye-adsorbed materials to be used as substrates in solid state fermentation (SSF) for protein enrichment.

3. 5. 2. 6. Membrane filtration

Membrane systems can be a good way to treat a large bulk of wastewater without the use of chemicals, but correct selection is vital when considering their use in textile plant. The method has the ability to clarify, concentrate and, most importantly to separate dye continuously from effluent (Xu and Lebrun et.al., 1999). It has some special features unrivalled by other methods; resistant to temperature, and adverse chemical environment, and microbial attack. The concentrated residue left after separation poses disposal problems and there are other disadvantages such us high capital cost, the possibility of clogging and membrane replacement. This method is suitable for water recycling within a textile dye plant.

3. 5. 2. 7. Ion exchange

Ion has not been widely used for the treatment of dye-containing effluents, manly due to opinion that ion exchanges cannot accommodate a wide range of dyes (Slokar and Le Marchel et.al., 1997). Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. In this way cation and anion dyes can be removed from dye-containing effluent. Advantages of this method include no loss of absorbent on regeneration, reclamation of

solvents after use and removal of soluble dye. Mayor disadvantage is cost. Organic solvents are expensive, and the ion exchange method is not very effective for disperse dye.

3. 5. 2. 8. Irradiation

Sufficient quantities of dissolved oxygen are required for organic compounds or material to be broken down effectively by radiation. The dissolved oxygen is consumed very rapidly and a constant and adequate supply is required. This has an effect on cost. Dye containing effluent may be treated in a dual-tube bubbling reactor. This method showed that some dyes and phenolic molecules can be oxidised effectively at a laboratory scale only (Hosono et.al., 1993).

3. 5. 2. 9. Electrokinetic

This is economically feasible method of dye removal. It involves the addition of ferrous sulphate and ferric chloride, allowing excellent removal of direct dyes from wastewater. There are poor results with acid dyes. This method consumes high cost of ferrous sulphate and ferric chloride and this method is not widely used. With this method production of large amounts of sludge occurs and this results in high disposal costs (Gahr et. el., 1994).

3. 5. 3. Biological methods

Biological treatments differ according to the presence or absence of oxygen. In the presence of oxygen the process is called aerobic (revival of biological sludge in aeration basins) and in the absence the process is called anaerobic (decay and rot in stabilising lagoons). A third way of biological treatment is call degradation by special fungi. Since biological treatment simulate degradation process that occur in the environment, it is also called biodegradation (Slokar and Le Marchel et.al., 1997). Biological activity is incapable of removing dyes effluent on a continuous basis. This is due to the time period of a few days required for the decolouration – fermentation processes. For industry, the dye – containing effluent must be held in large tanks and this present problems due to the sheer site size required.

3. 6. Theory and Practice of Membrane filtration

3.6.1. Basics of filtration

Membrane filtration as a means of purification or concentration relies on the principles that when the liquid passes across or through a physical barrier, particles whose size is larger than the pores in the membrane are retained on one side of the barrier, while the remaining liquid is allowed to pass through. Membrane processes do not destroy pollutants, they only separate them into a permeate and a concentrate. The retained fraction is known as the *concentrate or retentate*. The fraction passing through the membrane, driven by pressure, is the *permeate or filtrate*(Andersen et.al., 2005). The overall principle in any membrane separation is sketch in Figure 2:

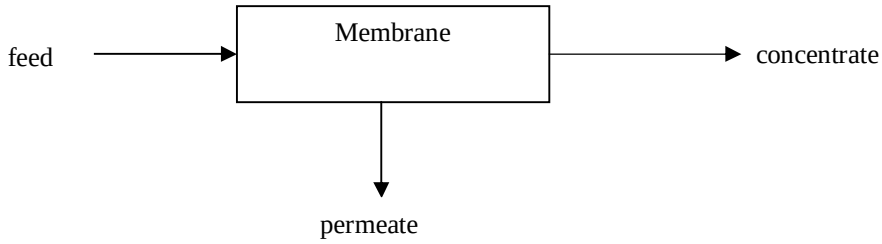

Figure 2: *The principle in membrane separation*

Membrane processes are very promising advanced treatment method for colour removal as well as reducing the volume of wastewater generated and recover and recycle valuable components from the waste stream. Membrane system has several advantages. They are compact and modular in addition to their selectivity and low energy consumption. Therefore, membrane units can relatively easily be incorporated into existing production sites. Furthermore, modern membranes present high resistance to heat, to acid aggressive chemicals and of micro-organisms. The unit for permeate production is "litre per square meter of membrane per hour", i.e. "Lmh" for short (Dvarioniene J. et.al., 2003).
Membrane technology (or membrane filtration) covers four different membrane groups: microfiltration, ultrafiltration, nanofiltration and reverse osmosis each having different characteristics (figure 3):

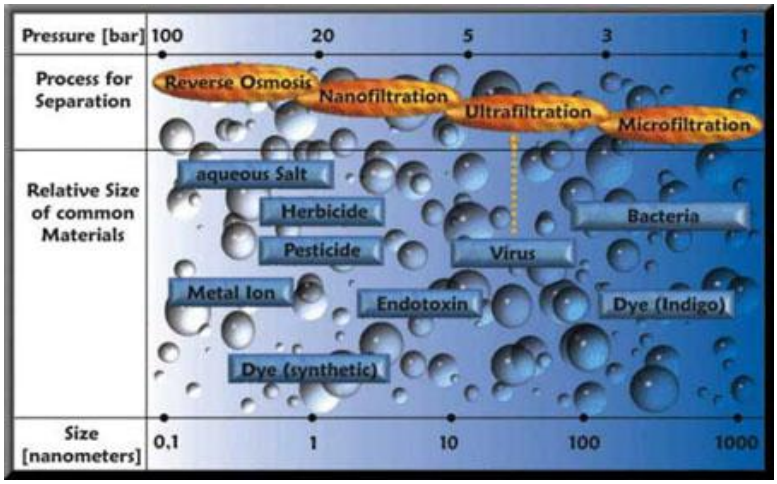

Figure 3: *Membrane filtration concepts. Source- internet*

Table 7 and 8 shows that separation of small particles/molecules requires a high trans membrane pressure. In addition, the rate of small particle/molecule size and consequently separation time and costs increases.

Table 7 *Overview of membrane processes*

Membrane process	**Dp (bar)**	**Size range (mm)**	**flux (L/m^2 h bar)**
Microfiltration	0.1 - 2.0	0.1 – 10	> 50
Ultrafiltration	1.0 - 5.0	0.02 - 0.3	10 – 50
Nanofiltration	5.0 - 20	0.001 - 0.01	1.4 – 12
Reverse osmosis	10 - 100	< 0.001	0.05 - 1.4

Table 8 *Type range for typical feed stream contents*

Species	**Dimensions (nm)**	**Molecular weight**
Yeast's and fungi	1000 - 10000	-
Bacteria	300 - 10000	-
Colloidal solids	100 - 1000	-
Proteins/polysaccharides	2 - 10	10^4 - 10^6
Enzymes	2 - 5	10^4 – 10^5
Organic molecules	0.3 - 0.8	30 – 500
Inorganic ions	0.2 - 0.4	10 -100
Water	0.2	18

The choice of the membrane system to be applied to the specific case study must be made in order to gain a good benefit/costs ratio and usually needs preliminary pilot-scale testing since textile wastewater usually are different from one mill to another. Three factors are of special importance for the selection of membrane for a particular separation:

- the pore size of the membrane, because it determines to a large extent what substances pass through membrane and what substances are retained.
- the membrane material, which determines chemical resistance and susceptibility to fouling and therefore the suitability for the various separations.
- the membrane shape, because it determines susceptibility to clogging, the cleaning efficiency and the pre-treatment required. The shape of membrane is essential to the proper and reliable operation of membrane filtration plant. The following membrane types are most frequently used: spiral wound, hollow fibre, tubular, plate and frame, and capillary.

3. 6. 2. Types of membrane filtration

There are four main classification of membranes, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and the finest of these, reverse osmosis (RO).

3. 6. 2. 1. Microfiltration (MF)

Microfiltration allows a simple clarification of the effluent, removing suspended particles (microorganism, inorganic particles, colloides). Common operation pressure is 2 bar or less and fluxes around 50 Lmh/bar. MF is suitable for removing colloidal dyes from the exhausted dyebath and the subsequent rinses. The auxiliary chemicals remain in the permeate (M. Marcucci et.al., 2002).

3. 6. 2. 2. Ultrafiltration (UF)

Ultrafiltration is primarily used in the separation particles and macromolecules higher then 10nm (bacteria, viruses and proteins). Common operation pressure is 1 – 5 bar or less with fluxes around 10 - 50 Lmh/bar. Treatment of secondary textile wastewater with UF produce the quality of permeate which allows wastewater reuse in the minor processes (rinsing, washing) of the textile industry, but it did not possess the requirements to be reused in delicate processes as dyeing light-coloured yarns (Marcucci M. et.al., 2001).

3. 6. 2. 3. Nanofiltration (NF)

Nanofiltration allows the separation of low molecular weight organic compounds and divalent salts, with an appreciable softening effect. Nanofiltration is applied when separation requirements are in the area between the optimum effectiveness of RO and UF, and high sodium rejection is not needed, but where other salts such as those of calcium and magnesium (i.e. divalent ions) or ions from solutes such as small molecules of sugar are to be removed. Common NF operation pressure from 5 – 20 bars and fluxes between 1.4 – 12 Lmh/bar (Dvarioniene J. et.al., 2003). In textile industry NF has been studied as treatment of secondary textile effluent after MF: the permeate was satisfactory and totally acceptable for water reuse (Marcucci M. et.al., 2001).

3. 6. 2. 4. Reverse osmosis (RO)

Reverse osmosis is suitable for removing ions and larger species from dyebath effluents. The permeate produced is usually colourless and low in total salinity. Normal RO operations pressure is from 10 -100 bars, expected fluxes are between 0.05 - 1.4 lmh/bar. The choice of membrane system to be applied to the specific case study must be made in order to gain a good benefit/costs ratio and usually needs preliminary pilot –scale testing since textile wastewater usually are different from one industry to another (Marcucci M. et.al., 2001).

3.6.3. Use of membrane filtration in textile industry

The textile dyeing industry demands large quantities of water, and results in large amounts of wastewater streams of complex contaminant matrix from the different steps of dyeing process. Because of more stringent regulations and economical advantages, companies tend to invest more and more time and money in water reuse. Purification is, therefore, advisable, in order to decrease the quantity of wastewater as well as to reduce water consumption.
Membrane filtration has been used for recycling process in textile industry for a long time. The early application of ultra filtration to polyvinyl alcohol (PVA) size recovery was accepted and used in full plant scale installation nearly 30 years ago (Rearick et. al., 1997).
Large textile mills continue to use membrane filtration techniques successfully today for this type of application. A system for the recovery of hot water, dyes, and auxiliary chemicals from textile waste streams was described by Porter and Goodman more then 20 years ago (Porter and Goodman et. al., 1984). The recovery of chemicals, energy and water for reuse is more economical today then it was years ago as fuel and energy costs increase and wastewater discharge regulation are much more demanding.
Wastewater reuse is particularly attractive for the textile industries in Italy, which is one of the most important fields of the Italian economy. The textile industry is a large user of water (typically 200-400L are needed to produce 1kg of fabric). Membrane filtration has been selected for the treatment and reuse of effluents mainly from textile dye baths (B. Van der Bruggen et. al., 2004). Membrane process have the potential either to remove the dyestuff and allow reuse of the auxiliary chemicals used for dyeing or to concentrate the dyestuffs and auxiliaries and produce purified water.

3. 7. Decolouration with UV/ H_2O_2

Combining UV radiation and hydrogen peroxide oxidation has been applied successfully in advanced oxidation processes (AOPs) to treat different pollutants in textile wastewater (Brodnjak et.al.2003).
Ultraviolet light is a catalyst and causes the dissociation of hydrogen peroxide into two hydroxyl radicals, represented in the following chemical equation, which cause the chemical oxidation of organic material:

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet}$$

Hydroxyl radicals degrade organics by taking away protons to generate organic radical compounds. These compounds are extremely reactive and are subject for further oxidation. Ultraviolet light alone has the ability to degrade organic compounds, but when ultraviolet light and hydrogen peroxide are combined, the overall oxidative reaction potential is greatly enhanced (Yang Y.,Travis, et. al., 1998)
Galindo and Kalt et.al. 1999, demonstrated that UV/H_2O_2 is able to destroy totally the chromophore structure of azo dyes and the reaction rate of azo dyes depends on the basic structure of the molecule and on the nature of auxiliary groups attached to the aromatic nuclei of dyes. The mechanism of dye destruction is based on the formation a very reactive hydroxyl radicals ($^{\bullet}OH$), that, with an oxidation potential of 2.8 V, can oxidize a broad range of organic compounds.(Aleboyeh A., et. al., 2003). The UV/H_2O_2 process has additional advantages and also disadvantages (Majcen, et.al., 1997, 2003), which are presented in table 9:

Table 9 *Advantages and disadvantages of decolouration with UV/H_2O_2 process*

Advantages	**Disadvantages**
no sludge formation	not applicable for all dye types
no salt formation	requires separation of suspended solid particles
considerable safety, easy operation	
short reaction times	
reduction of COD	

3. 8. Constructed wetland (CW)

Constructed wetlands are a new approach for decreasing environmental pollution, based on biological purification of wastewaters with helophytes planted in a CW. CW offer an effective and economical solution to the growing problems of environmental pollution. They are simple in concept, inexpensive to construct and easy to operate. Constructed wetlands are build as a part of the natural local environment which they successfully preserve by protecting it against pollution (Vrhovšek D., Bulc, et.al.1994).
The CW with the horizontal subsurface flow of wastewater is composed of one or more beds, filled with substrate, enabling the growth of selected plant species and micro organisms. The bottom of the bed is fortified with impermeable layer. The substrate is directly involved in eliminating pollutants with physico chemical interaction such as filtration and sedimentation of suspended solids, filtration of pathogenic organism, sorption of organic matter, nitrogen, phosphorus and heavy metals. (Vrhovšek D., et.al. 1996).
Indirectly the substrate act as a support for root system and as a surface area for the adhesion of micro organisms. Micro organisms are the main agents of purification in CW. They use organic matter as the energy reach substrate and transform it into nutrients and energy (Marin and Moshiri, et.al.1994).
Vegetation plays an important role since the diffusion of oxygen from roots creates conditions needed for the development of micro organisms, which participate in the aerobic decomposition of organic matter. The extensive root system serve as a large surface area for development of microorganisms and enable filtration as well as adsorption of sediment Matter (Vrhovšek D., et.al. 1996).
Due to numerous factors influencing the process dynamics in CW, the system can not be regarded as a “black box” and thus, in spite of an increasing theoretical and empirical knowledge about CW, general instructions for design and operation can not be offered yet (Urbanc-Bercic, et.al. 1995).

4. INTRODUCTION OF THE COMPANY TEKSTINA D.D.

The Tekstina company employs 390 people. Manufacturing process begins with raw fibres (cotton, polyester, viscose) and ends with finished woven fabric. The main fibre used is cotton, which is manufacture through three mills: spinning, weaving and finishing mill and each mill have different manufacturing operations (table 10) ;

Table 10 *Manufacturing process from row fibres to finished woven fabric*

SPINNING MIIL	WEAVING MILL	FINNISHING MILL
opening bale and blending	warping	desizing
carding	sizing	scouring and washing
spinning	weaving	mercerising and washing
	inspecting	bleaching and washing
		dying and washing (fabric and yarn)
		printing
		finishing
		inspecting

4. 1. Water usage and effluent production

Tekstina requires water for cooling system, air conditioning, steam generation, process water and for personnel consumption and sanitation. (table 11)

Table 11 *Water usage in Tekstina*

	Annual water quantity (m^3)
Water sources :	
- from waterworks (drinking water)	29 573
- from own water capture(industrial water)	495 443
Total water supply	525 016
Water consumption:	
- cooling and air conditioning	121 000
- process water	112 066
- waste water used in production + sanitary water	291 950
Total water consumption	525 016

- **cooling and air conditioning water:**

The process in spinning and weaving mill requires 50- 85 % relative humidity, and to assure this conditions, cooling and air conditioning are required. During summer months, the water is used also for cooling. Total annual consumption for cooling and air conditioning in spinning and weaving mill is approximately 233.066 m^3 water. From this quantity 112.066 m^3 of water is used in process and 121. 000 m^3 of water is discharge to river Hubelj.

- **steam generation :**

Tekstina produce steam with steam boiler EMO 12.5 from industrial water. Steam is manly used in finishing department for heating.

- **personnel consumption and sanitation**

Drinking water from waterworks is used for sanitation, cooking and for fire department. Total water consumption is 29 600 m^3 and water is discharged to municipal sewer.

- **process water**

Industrial water is manly used in the finishing department for desizing, scouring, mercerising, bleaching, dying (fabric and yarn), printing and finishing. During the finishing process, 262.400 m^3 of waste water is generated. Daily waste water production is 1100 m^3/day and of this part is approximately 100 m^3/ day is intensely coloured wastewater. Waste water from the finishing mill is alkaline (pH 10 - 12) and is intensely coloured. Mainly reactive dyes are used for dying, but reductive, pigment and disperse dyes are used also. The potential pollutants from wet processing operations are: NaOH, H_2O_2, dyes, salts, starch and derivates, waxes, antistatic agents, surfactants, soaps, softeners, urea, metals etc.

The wastewater from the dyeing process is characterised by:

- **high content of dyestuff;** reactive dyes are typically azo-based chromophores combined with different types of reactive groups. The relative large chromophores place reactive dyes in the molar mass range of 700 - 1000 g/mol. The reactive groups can be based on dichlortriazin or vinyl sulphonic acid and will be negatively charged. Beside the reactive groups, other negatively charged groups are found – typically sulfonic acid groups. The reactive groups react with hydroxyl groups in the cellulose fibre during the dyeing reaction. However, a relatively large part of the reactive groups will react with water leaving the dyestuff at an unreactive form. Due to the properties of the chromophore, the dyestuff is quite adsorptive to the cellulose, and hydrolysed dyestuff requires large amounts of water, preferably at high temperature, in the proceeding rinses to be properly washed out
- **salts**; salinity in the dye bath typically varies between 40,000 - 80,000 mg/L. In the proceeding rinses, salinity will decrease typically by a factor of 3 for the batch wise rinse and much more by the very water consuming “overflow” rinse.
- **COD**; deriving from additives such as acetic acid, detergents and complexing agents, suspended solids including cotton fibres. Various kind of dispersing and complexing agents are used in rinsing and the last subsequent softening of the textiles. Some of these have been found to be cationic and based on quaternary ammonium ions.
- **high temperature**; at pH above 10 and temperature above 50-60°C, certain types of reactive dyestuffs are sensitive to breaking the covalent bond to the cellulose. Therefore, the dye bath (having the pH > 10), and the first batch rinse to follow need a temperature not higher than 50 - 60°C. After this first rinse, a temperature of 90 - 95°C is preferable for the rinsing. For economical reasons, some of the rinses are often kept colder.
- **pH**; typically above 11 in the dyebath followed by neutralization with H_2SO_4.

Wastewater from the process of finishing is collecting in the pool for neutralizing with H_2SO_4 to pH value 6,5 - 9,5 and it is discharge to municipal sewer. UV/Vis spectra of typical wastewater from Tekstina is presented in Figure 4.

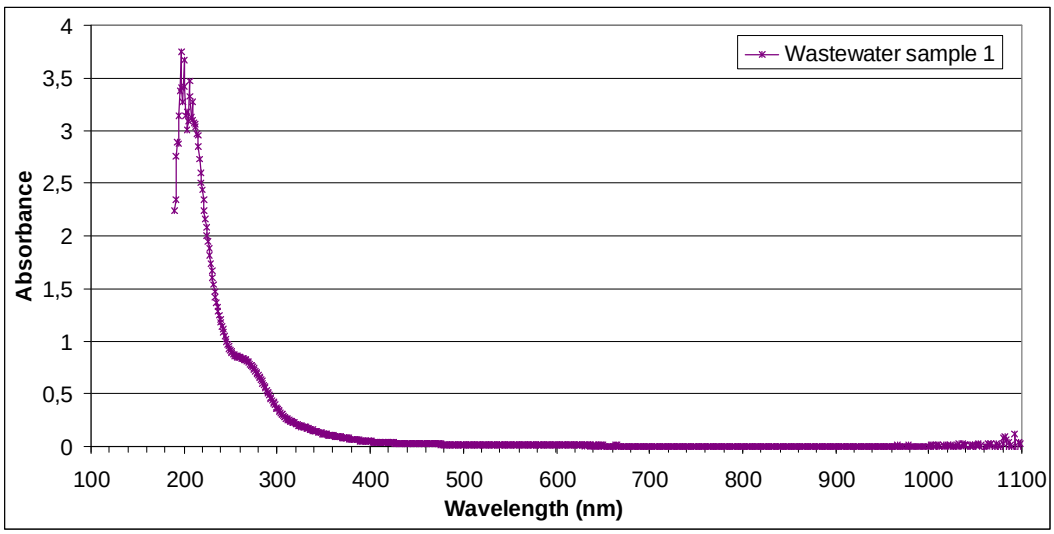

Figure 4: *UV/Vis spectra of typical wastewaters from Tekstina*

4. 2. Monitoring of wastewater

In order to meet legislation requirements, Tekstina must carry out monitoring of wastewater by the independent institution Hidroinžiniring d.o.o. In the table below are presented 6 sampling points for the year 2004 with average value and allowed values for discharge to waterway or to municipal sewage treatment plant.

Table 12 *Monitoring of the waste water from company Tekstina for the year 2004*

			Allowed outflow to		Sampling point						Average
No.	Parameter	Unit	waterways	sewage	1	2	3	4	5	6	value
	date		-	-	29.3.04	27.5.04	28.6.04	21.7.04	15.9.04	2.12.04	/
	time		-	-	14:25	13:57	15:00	18:22	16:40	10:10	/
	volume	m^3	-	-	1511	1393	1607	1514	1536	1264	1471
1	temperature	^oC	30	40	27,1	27,0	27,0	28,8	29,0	31,5	28,4
2	pH		6,5 - 9,0	6,5- 9,5	8,75	8,55	8,24	6,92	7,19	9,35	8,0
3	suspended solids	(mg/l)	80	-	89	93	88	115	121	148	109
4	COD	(mg/l)	200	-	439	213	345	498	494	496	414
5	BOD_5	(mg/l)	30	-	122	60	122	198	212	173	148
6	Cu	(mg/l)	1	1	0,05	0,05	0,05	0,05	0,05	0,05	0,05
7	Cd	(mg/l)	0,1	0,1	0,005	0,005	0,005	0,005	0,005	0,005	0,005
8	Cr (VI)	(mg/l)	0,1	0,1	0,01	0,01	0,01	0,06	0,01	0,01	0,02
9	Pb	(mg/l)	0,5	0,5	0,05	0,05	0,05	0,05	0,05	0,05	0,05
10	AOX	(mg/l)	0,5	0,5	0,16	0,24	0,41	0,58	0,03	0,26	0,28
11	Total P	(mg/l)	1	-	1,53	1,37	2,32	2,08	1,98	2,17	1,91
12	colour 436 nm	m^{-1}	7	-	2,3	3,6	0,5	1,7	1,2	2,8	2,0
13	colour 525 nm	m^{-1}	5	-	2,4	2,4	6,5	2,4	0,96	2,8	2,91
14	colour 620 nm	m^{-1}	3	-	2,3	1,9	5	1,7	0,89	2,9	2,45
15	Al	(mg/l)	3	-	0,2	0,4	0,1	0,2	0,1	0,2	0,2
16	Zn	(mg/l)	3	3	0,1	0,1	0,1	0,1	0,1	0,1	0,1
17	Co	(mg/l)	1	1	0,01	0,01	0,01	0,01	0,01	0,01	0,01
18	Sn	(mg/l)	1	1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
19	Total Cr	(mg/l)	2	2	0,05	0,05	0,05	0,05	0,05	0,05	0,05
20	Cl_2	(mg/l)	0,2	0,5	0,1	0,1	0,1	0,1	0,1	0,1	0,1
21	Total Cl_2	(mg/l)	0,5	1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
22	Sulphate - SO_4	(mg/l)	/	400	280	250	70	64	350	650	277
23	Sulphide- S	(mg/l)	0,5	1	0,05	0,05	0,05	0,05	0,05	0,05	0,05
24	Sulphite- SO_3	(mg/l)	1	10	0,5	1,2	1,4	0,5	0,5	0,5	0,8
25	TOC	(mg/l)	60	-	120	43	91	140	160	9	94
26	Total hydrocarbons	mg/l	10	20	0,1	0,3	0,1	0,1	0,1	0,2	0,2
27	LKCH	mg/l	0,1	0,2	0,01	0,01	0,01	0,01	0,01	0,01	0,01
28	Phenols C_6H_5OH	mg/l	0,1	10	0,03	0,02	0,11	0,07	0,07	0,13	0,07
39	Total tensides	mg/l	1	-	0,6	1,5	1,0	40	2,4	4,0	8,3

4. 3. Water consumption and water costs

The water comes to the factory Tekstina from two sources (figure 5). The first source (495.443 m^3/y) is from own water capture and is used for production as industrial water. The second source (29.573 m^3/y) is drinking water and is manly used for sanitation and cooking. After the use in production (112.066 m^3/y), the water is collected in two streams:

- the first one, 291.950 m^3/y, collects all polluted waste water from finishing and weaving department and is discharge to municipal sewage treatment plant.
- the second one, 121.000 m^3/y of cooling water, is directly discharged to a river Hubelj.

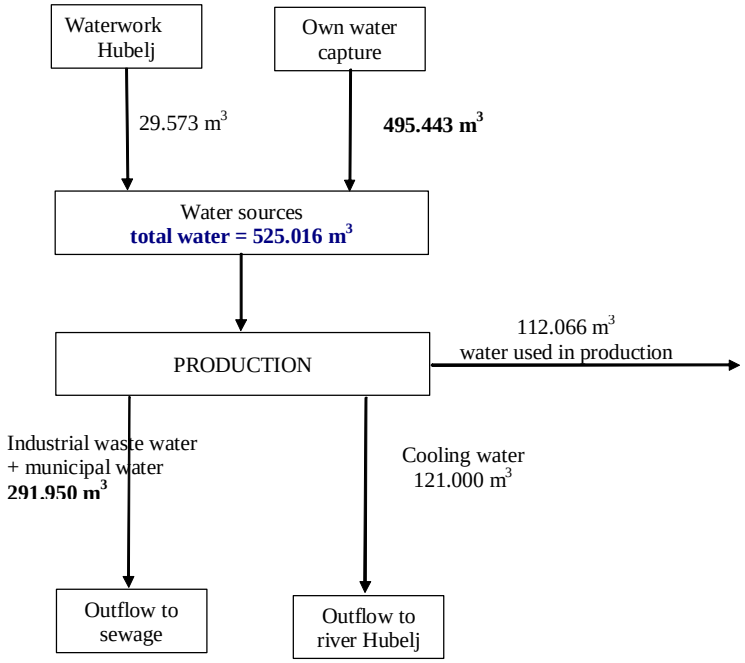

Figure 5: *Water flow in Tekstina company (data from the year 2004)*

The annual costs for the total water consumption of 525.016 m^3 are 270.639,55 € at present, and are stated in the table 13. The present cost for wastewater treatment is 204.365,00 €. The ecological tax is 18.385,79 € and is dependant of water pollution and water taxes for each community. The cost for drinking water from waterworks (16.856,61 €) and cost for industrial water (24.772,15 €) is becoming more expensive from year to year and this compels the company Tekstina to solve the ecological problems which are tightly connected with high water costs.

Table 13 *Water cost for company Tekstina for year 2004*

		unit	cost	total
Total water consumption	525.443,00	m^3/y		
Industrial water (own water capture)	495.443,00	m^3/y		
Drinking water (waterwork)	29.573,00	m^3/y		
Cost for industrial water	495.443,00	m^3/y	0,05 €	24.772,15 €
Total quantity of wastewater	291.950,00	m^3/y		
Ecological charge (EO)	707,69	/		
Tax	25,98	€		
Ecological charge (EO)	707,69	/	25,98 €	18.385,79 €
Cost for wastewater treatment	291.950	m^3/y	0,70 €	204.365,00 €
Cost for monitoring	6.260,00	€		6.260,00 €
Cost for water from waterworks	29.573,00	m^3/y	0,57 €	16.856,61 €
Total water costs				**270.639,55 €**

5. EXPERIMENTAL PART

5.1. Selection of the best available technologies for wastewater treatment

Water resources management has become an important issue, and selection of the right cleaning technology can provide financial saving as well as help meet present and future environmental legislation. In this work, three different advanced technologies have been selected according cleaning techniques (physical, chemical, and biological):

- membrane filtration with reverse osmosis (RO)
- remediation with contracted wetland (CW)
- oxidation with H_2O_2 + UV

Experiments have been performed at three different pilot plants to improve the quality of wastewater from company Tekstina d.d.

5. 2. Reverse osmosis plant (RO)

5. 2. 1. Materials

The experiment has been performed on reverse osmosis using open channel disc tube module DT manufactured by Pall Rochem, Wassertechnik Gmbh, Hamburg. Reverse osmosis plant is located at Stara Gora Landfill.
The modular design consists of individual thin film composite membranes cushioned between hydraulic cover disks, stacked, and assembled about a centre tension rod and sealed between metal end flanges.
Wastewater flows down passages between the disc stack and the pressure vessel and enters the flow chamber from beneath the bottom disk. The flow is directed up and over each membrane cushion allowing pure water to pass through the semi-permeable membrane and be collected by the permeate collector. Contamination by feed water is prevented by 'O' ring seals fitted to the hydraulic disks. As the pure water is removed, the strongly concentrated feed is taken away to discharge. The open channel created by the membrane cushion enables fully turbulent feed water and permeate flow. (See figure 6, 7)

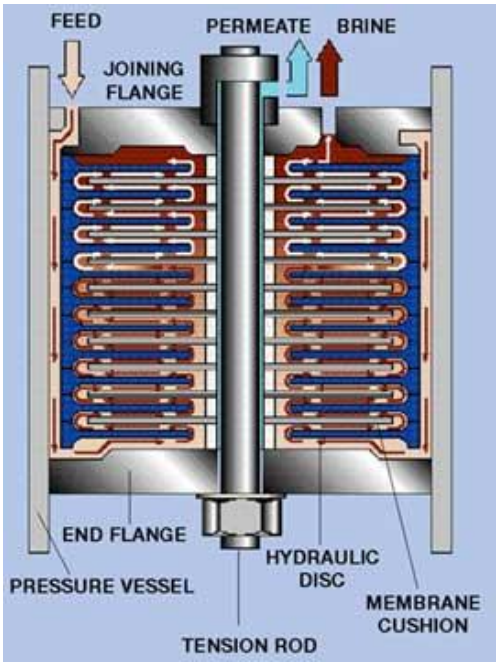

Figure 6: *Construction profile of TD modul. Source-Pall Rochem Wassertechnik Gmbh, Hamburg*

At the beginning of the test, the waste water was poured into a storage tank 1 from where it was pumped through the prefiltration unit to the open channel disc tube module DT at an average pressure of 8, 5 bar. About 80 % of feed volume was separated as permeate to storage tank 2. The 20 % of the feed volume was collected in storage tank 3 as retentat (concentrate). The average pressure of permeate during the experiment was 8.4 bar and average permeate flow was 0.46 m^3/h.

Figure 7: *TD modul. Source-Pall Rochem Wassertechnik Gmbh, Hamburg*

5. 2. 2. Methods

The experiment program started in April 2004. Sampling of wastewater, 30m^3, was transported by tanker from company to Landfill Stara Gora. Performance of membrane filtration with reverse osmosis has been evaluated by investigation of the following parameters: pH, conductivity, COD, BOD_5 spectral absorption coefficient (SAC), sulphate. The pilot plant has on-line measurements of pH and conductivity.

Sample analyses were performed according to standard methods in laboratory of wastewater treatment plant (WTP) in Ajdovščina and laboratory at University of Nova Gorica. In the table 14 are presented testing methods and testing equipments for evaluation of the following parameters:

Table 14 *Analyses performed in testing laboratories according testing methods*

Parameter	Testing method
Chemical Oxygen Demand (COD)	SIST ISO 6060
Biochemical Oxygen Demand (BOD_5)	SIST ISO 5815
Special Absorbance Coefficient (SAC)	ISO 7887
Sulphate ($S0_4$)	DIN EN ISO 10304-1

Because of the technical problems on the RO plant, the experiment has been performed only once. The experiment was documented through the figures 8 - 10. The results of this test are present in Section 6.1 on pages 30 - 32.

Figure 8: *Filling of tanker with waste water at company Tekstina. Source-photo Lucija Kobal, 2004.*

Figure 9: *Reverse osmosis plant at Landfill Stara Gora. Source- photo Lucija Kobal, 2004.*

Figure 10: *Emptying of tanker to reservoir of Reverse osmosis plant. Source- photo Lucija Kobal, 2004.*

5. 3. Constructed wetlands pilot plant

5. 3. 1. Materials

Wetland pilot plant is located at the wastewater treatment plant (WTP) in Ajdovščina. The system consist of three beds. Bed A and B have function of filtration, while bed C has a cleaning function . Figure 11 shows the scheme of the system:

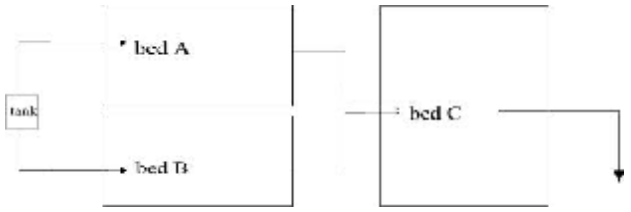

Figure 11: *Scheme of wetland pilot plant construction*

The bottom of beds was fortified with 2 mm thick HDPE (high density polyethylene) foil dimension 6,5 x 10 m to ensure impermeability (producer Sinteza Celje). Media consist of gravel and sand and are composed as follows:

Bed A: dimension: 5 m long and 4 m wide
12 m^3 fine sand, grain size 0-4 mm
12 m^3 sand, grain size 4-8 mm

Bed B: dimension: 5 m long and 4 m wide
12 m^3 fine sand, grain size 0-4 mm
12 m^3 sand, grain size 4-8 mm

Bed C dimension: 5 m long and 8 m wide
14 m^3 fine sand, grain size 0-4 mm
14 m^3 sand, grain size 8-16 mm
5,5 m^3 gravel, grain size 16-32 mm

Out flows of the basins A an B are equipped with out flow-valve for flux regulation to basin C. Regulation of inflow of waste water from the tank to basin A and B is regulated with inflow-valve.

The wetland pilot plant was planted in spring with young shoots of *Phragmatis australis*. All three basins have been planted with density 6 pieces/m^2 and during experiment filled with wastewater from Tekstina plant. The wastewater filters by gravity through the beds, where it is cleaned by the plant roots and micro organisms.

The experiment was documented through the figures 12-15.

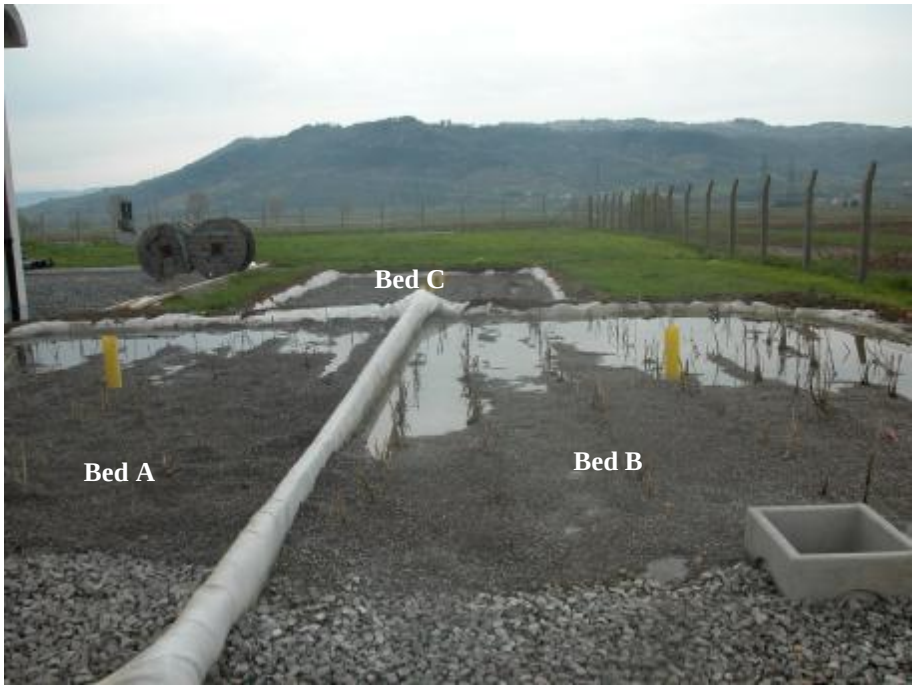

Figure 12: *Wetland pilot plant planted in April with young plants of Phragmatis australis. Source- photo Lucija Kobal, 2004.*

Figure 13: *Wetland pilot plant in August with plants of Phragmatis australis. Source-photo Lucija Kobal, 2004.*

Figure 14: *Closer look of Phragmatis australis plan. Source- photo Lucija Kobal, 2004.*

Figure 15: *Regulation of inflow of waste water from the tank to basin A and B is regulated with inflow-valve. Source- photo Lucija Kobal, 2004.*

5. 3. 2. Methods

The experimental program at Ajdovščina began in May 2005 and ended in September 2005 in cooperation with Limnos (Nekrep I. et.al 2006) and Textile Department, Faculty of Mechanical Engineering University of Maribor where all parameters have been measured. Efficiency of CW was measured at different values of hydraulic load (1l/min, 5 l/min and 10 l/min).
Waste water from Tekstina has been taken from neutralisation pool and was transported by tanker having a volume of 5000 L every month to the wetland pilot plant. Sampling was carried out at inflow into CW and at the outflow of the basin C.

Parameters measured and used for evaluation of the wastewater quality before and after purifying process were: pH, temperature, TSS, COD, BOD_5, NH_3-N, NO_3-N, NO_2-N, org. N, tot. N, tot. P, absorbance at three wavelength (436 nm, 525 nm, 620 nm), SO_4, Cl, AOX; TOC. Sample analyses were performed according to standard methods in laboratory of wastewater treatment plant (WTP) in Ajdovščina and laboratory of Textile Department, Faculty of Mechanical Engineering University of Maribor. In the table 15 are presented testing methods and testing equipments for evaluation of the following parameters:

Table 15 *Analyses performed in testing laboratories according testing methods*

Parameter	**Testing method**
pH	SIST ISO 10523
Temperature	DIN 38404-C4
Suspended solids	ISO 11923
Chemical Oxygen Demand (COD)	SIST ISO 6060
Biochemical Oxygen Demand (BOD_5)	SIST ISO 5815
Nitrate–nitrogen ($N0_3$-N)	Spectrophotometric method with Na - silicate
Nitrite nitrogen ($N0_2$-N)	EN 26777: 1993
Nitrogen- Determination of Kjeldahl nitrogen	SIST EN 25663
Total phosphorus	SIST ISO 6878-1
Ammonia nitrogen	SIST ISO 57664
Spectral Absorbance Coefficient (SAC)	ISO 7887
Sulphate ($S0_4$)	DIN EN ISO 10304-1
Absorbance Organic Halogen (AOX)	SIST ISO 9562
Total Organic Carbon (TOC)	SIST ISO 8245

The results of this test are present in Section 6.2 on pages 32 – 47.

5. 4. Hydrogen peroxide /UV pilot plant

5. 4. 1. Materials

Decolourisation with H_2O_2 /UV was performed at a pilot plant manufactured by Solvay Interox (figure 16) which is located in Textile Department, Faculty of Mechanical Engineering University of Maribor. Technical characteristic of computer controlled pilot plant are: volume of reservoir is 6 L, Hg ultraviolet lamp emits at wavelength 256 nm (Puv = 400-2000 W), flux inside of pilot plant is 3 l/min. At higher temperatures, the power of UV lamp became weaker. For this reason, it became necessary to install a cooling system.
The purpose of experiment was to take advantages of thermal energy gained by the waste water after the process of dying. This energy was used for the activation of hydrogen peroxide and at the same time for partial decolouration of waste water. The temperatures after the process of dying are different according to the type of fibres;

- temperature of dye bath out flow for cotton dying is 60°C
- temperature of dye bath out flow for man-made fibres dying is 60-90 °C

After thermal activation, hydrogen peroxide was activated with UV light till the decolouration was complete (Figure 16). Before thermal decolouration TOC was measured.

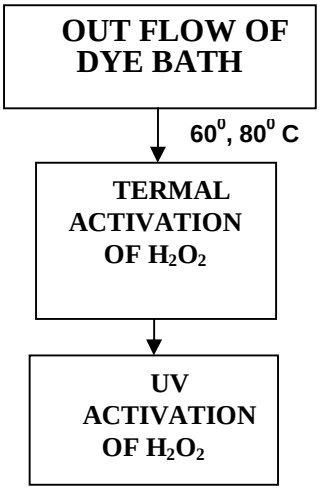

Figure 16: Termal/UV/H_2O_2 process

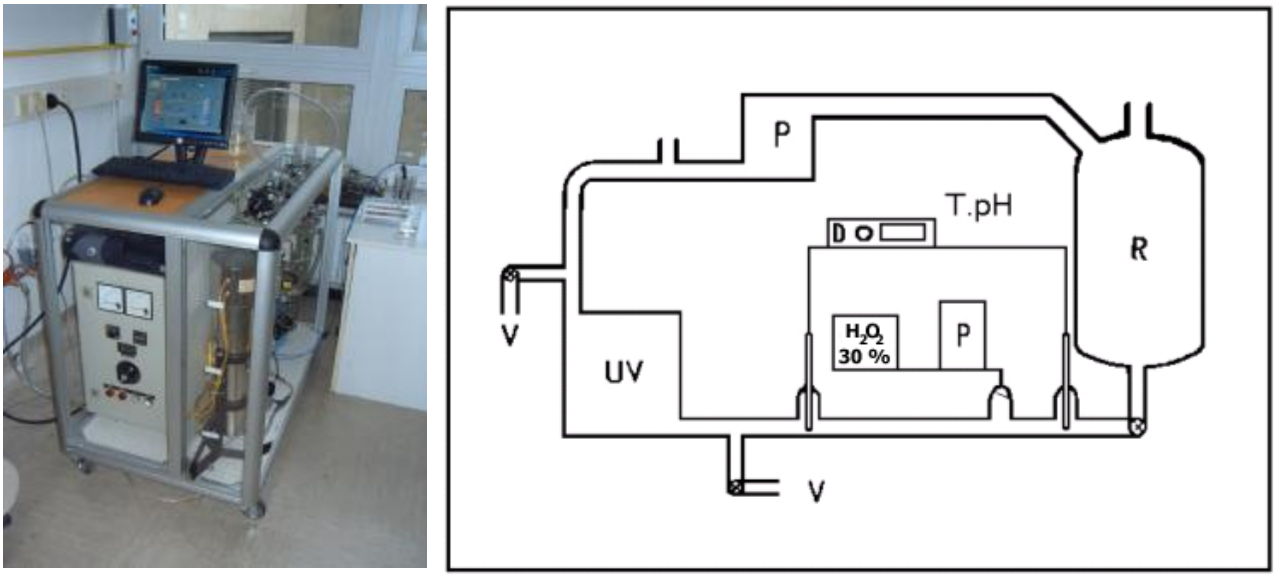

Figure 17: *Photo and schematic of Solvay Interox pilot plant; P = pump, UV= UV reactor, R = reservoir with waste water,$H_2O_2$30%=hydrogen peroxide with 30% concentration, V= sample draw. Source- Majcen-Le Marechal, 1997.*

5. 4. 2. Methods

The experimental program began in May and ended in late June of 2005 in cooperation with Textile Department, Faculty of Mechanical Engineering University of Maribor. Sampling of waste water from Tekstina was transported every week to Maribor where all experiments took place.
A volume of 6 L of wastewater effluent was pumped into reservoir, the water flow was 3 dm^3/min, the dosage of hydrogen peroxide was 4.5 ml/L, and the UV lamp (λ= 254nm) was set to 1400 W.
Experimental conditions are stated in the table 16:

Table 16 *Experimental conditions of decolouration with termal/UV/ H_2O_2 process*

Procedure	Volume of sample (L)	Catalyst	Volume H_2O_2 (ml/l)	Temperature (°C)	Power of UV lamp (W)	pH
Thermal	6	Yes	10	80	/	3
UV	6	No	8,3	20-35	1600	2-3

The pilot plant have on-line measurements the following parameters; conductivity, pH, temperature, decolouration at three wave length (436 nm, 525 nm, 620 nm) and TOC. For experiment we used 30 % concentration of H_2O_2.
The results of this test are present in Section 6.3 on pages 47 – 51.

6. RESULTS

6. 1. Results of decolouration of wastewater with process of reverse osmosis (RO)

Sampling of textile effluent was performed only once in order to test efficiency of the pilot plant for the measured parameters; COD, BOD_5, sulphates, decolouration at three wavelength 436, 525, 620 nm. All measurements were preformed at the average flux 0,46 m^3/h, conductivity 5,62 mS/cm, pressure 8,4 bar.
The reverse osmosis permeate has good results of wastewater purification: the COD values were reduced by up to 98%, the BOD_5 values up to 99%, the SO_4 values up to 99%, decolouration at wavelength 436 nm up to 97%, decolouration at wavelength 525 nm up to 98% and decolouration at wavelength 620 nm up to 86 %. The average purification on RO pilot plant of waste water was extremely high 96% (figure 18).
In figures 19–24, are values of measured parameter before and after purification on RO pilot plant are presented separately.

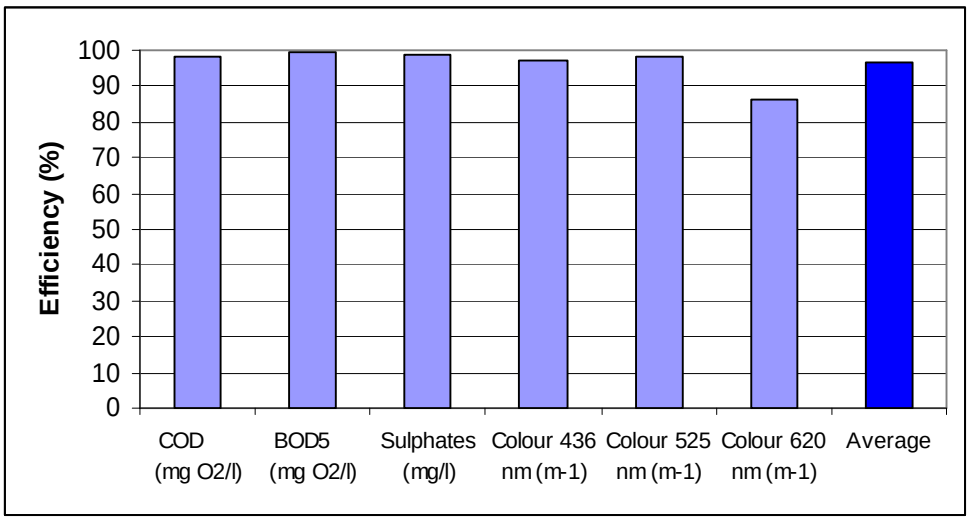

Figure 18: *Efficiency of purification of textile wastewater for measured parameters (COD,* BOD_5*, Sulphates, decolouration at three wavelength 436, 525, 620 nm and average of all parameters) on RO pilot plant, April 2004*

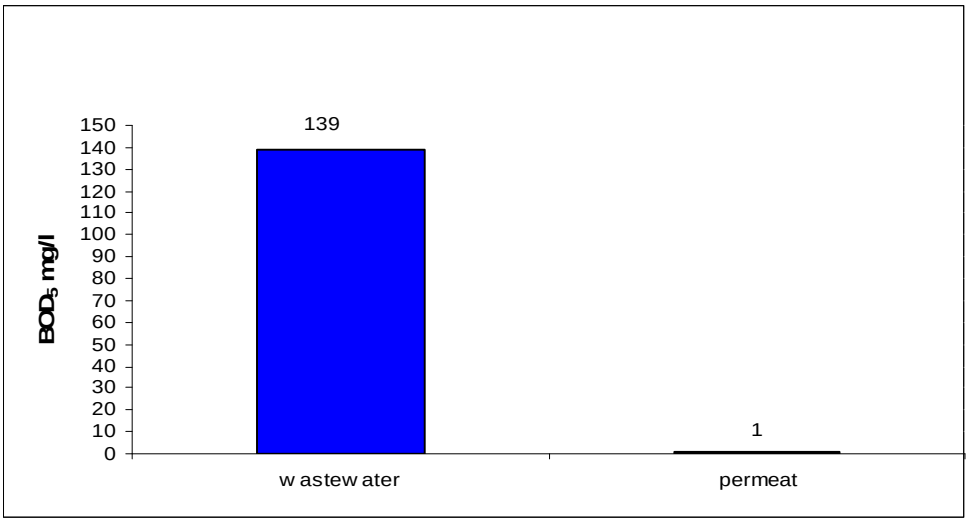

Figure 19: *Result of BOD_5 values of the waste water at inflow and outflow of RO pilot plant, April 2004*

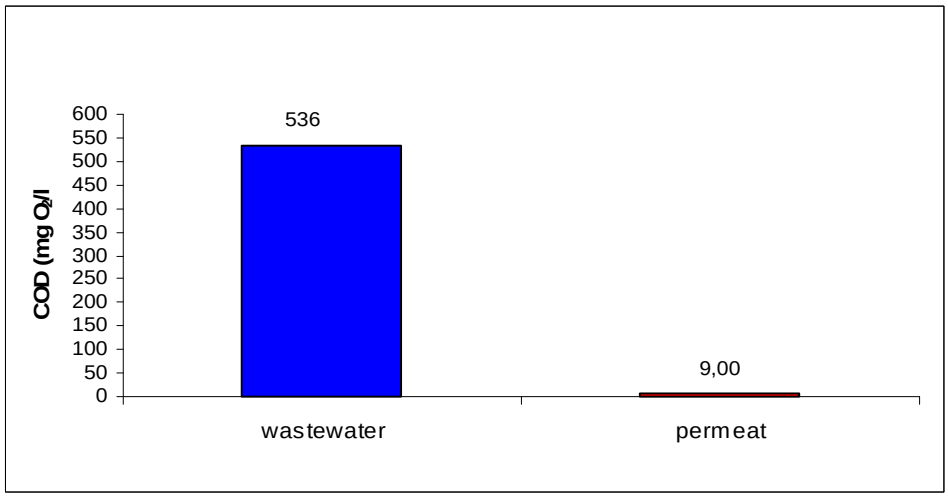

Figure 20: *Result of COD values of the waste water at inflow and outflow of RO pilot plant, April 2004*

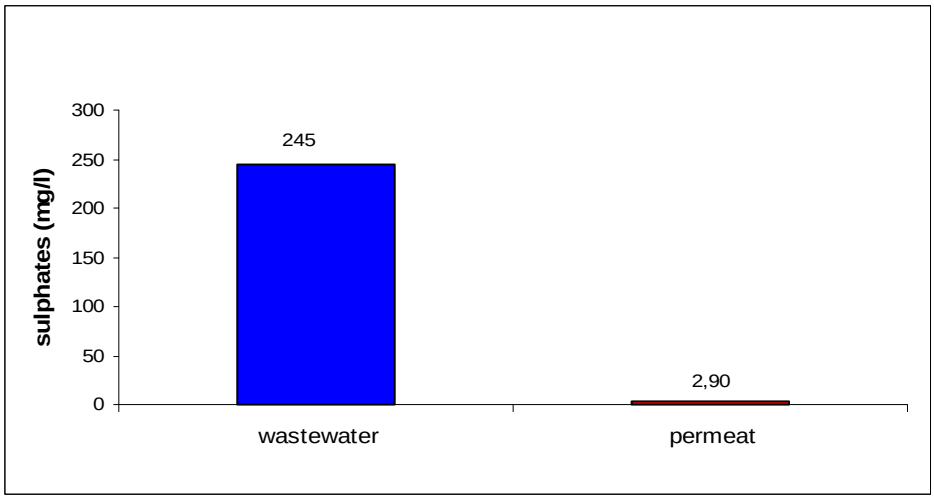

Figure 21: *Result of sulphates values of the waste water at inflow and outflow of RO pilot plant, April 2004*

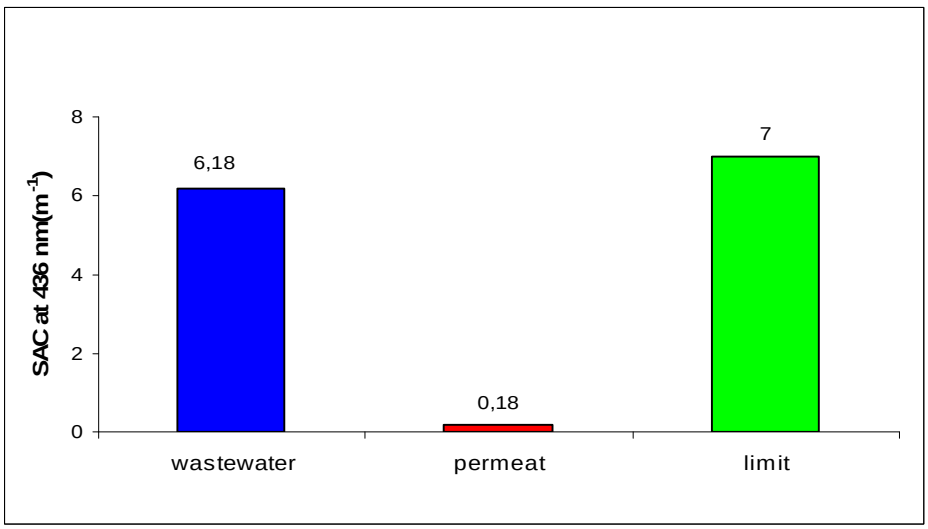

Figure 22: *Result of wastewater decolouration at wavelength 436 nm at inflow (wastewater), outflow (permeate) and limit value of RO pilot plant, April 2004*

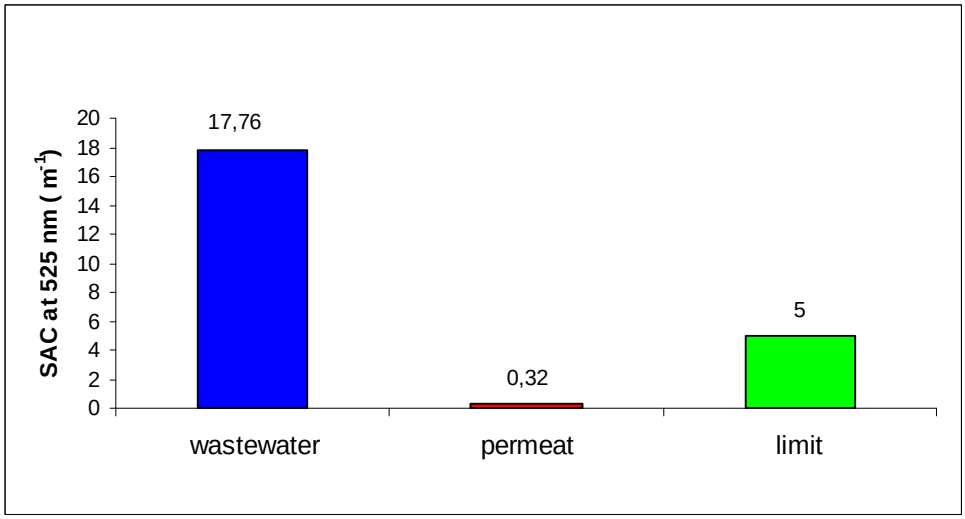

Figure 23: *Result of wastewater decolouration at wavelength 525 nm at inflow (wastewater, outflow (permeate) and limit value of RO pilot plant, April 2004*

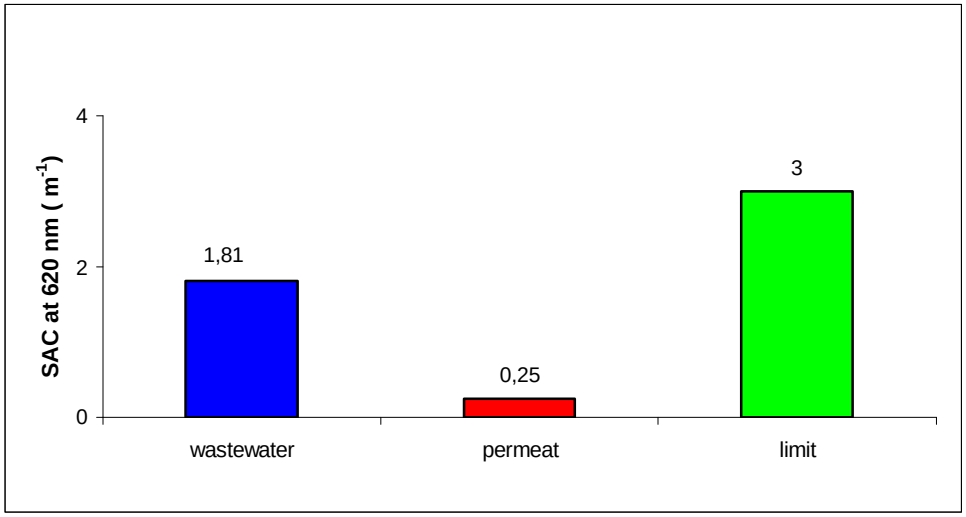

Figure 24: *Result of wastewater decolouration at wavelength 620 nm at inflow (wastewater, outflow (permeate) and limit value of RO pilot plant, April 2004*

6.2. Results of decolouration of wastewater with biological purification of wastewaters with helophytes planted in constructed wetland (CW)

The results contained in the figures 25 - 52 present inflow and outflow values of the following parameters: suspended solids, BOD_5, COD, TOC, AOX, NH_3-N, NO_3-N, NO_2-N, total nitrogen, total phosphorus, SO_4 values, and decolouration at wavelength 436 nm, 525 nm, 620 nm. Results of this research show parameters for waste water on constructed wetland (CW) at different values of hydraulic load during the sampling period May to September 2005.

Figure 25 present efficiency of all measured parameters on constructed wetland in sampling period from May to September 2005.

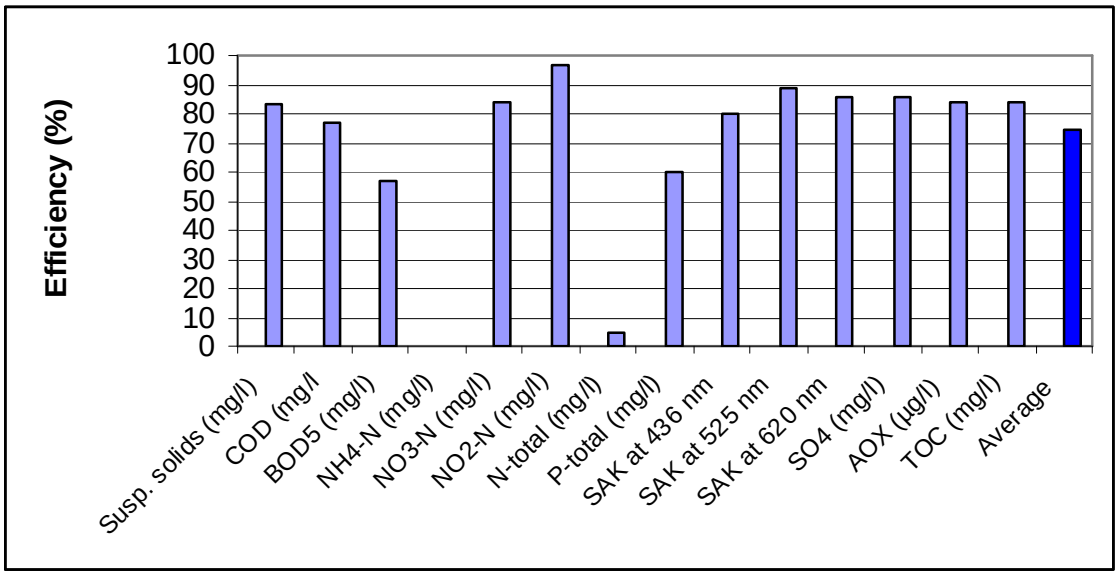

Figure 25: *Efficiency of purification of textile wastewater for measured parameters (suspended solids, COD, BOD5, NO3-N, NO2-N, N-total, P-total, SO4 values, decolouration at wavelength 436 nm, 525 nm, 620 nm and average of all parameters on constructed wetland (CW), sampling period May to September 2005.*

Figure 26,27 present values of suspended solids and showing large variations at inflow (from 27 to 408 mg/l) and small variations at out flow (from 7 to 11mg/l).The highest reduction of suspended solids was obtained at hydraulic load 1 l/min (May), with efficiency 98%. Efficiencies of reduction for suspended solids range from 32 to 98 %. Average reduction of suspended solids was 83 % (figure 27)

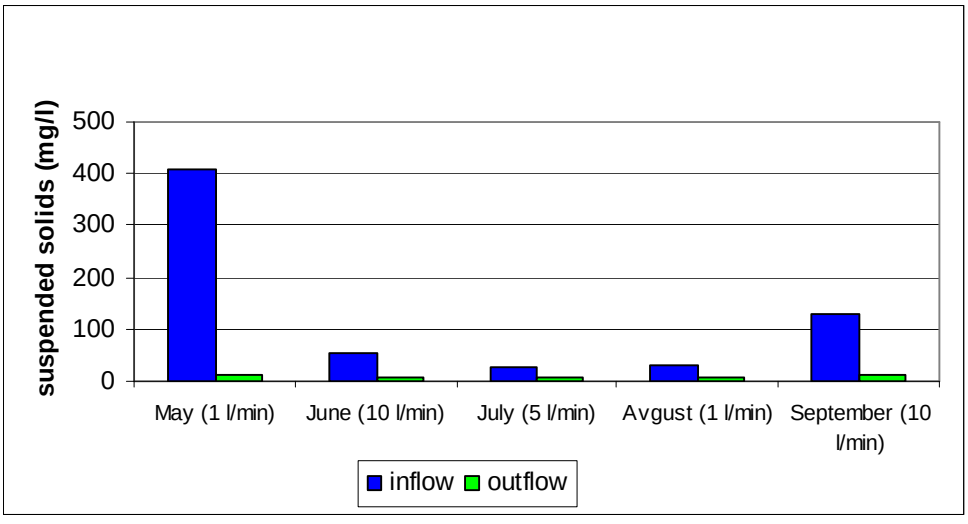

Figure 26: *Result of suspended solids in waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005.*

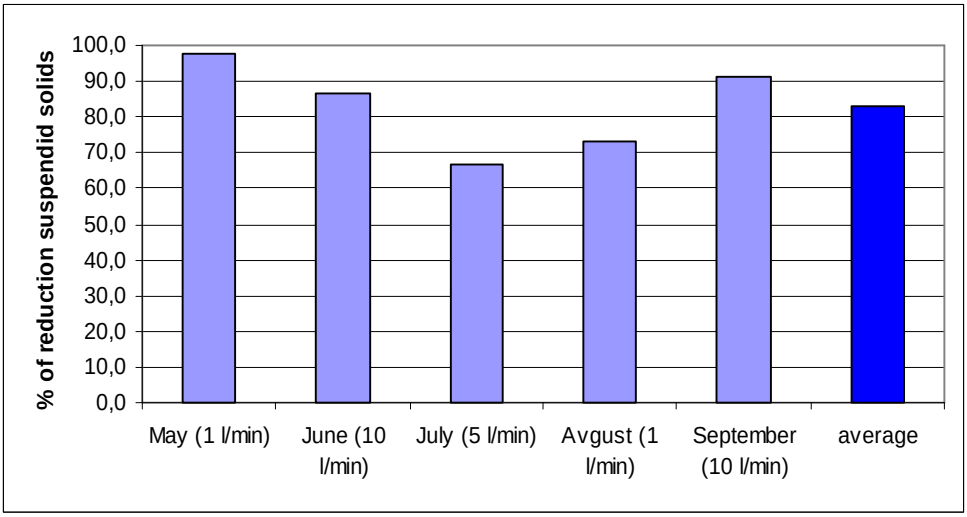

Figure 27: *% of reduction suspended solids in waste water at outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figure 28, 29 present BOD_5 values showing large variations at inflow (from 98 to 350 mg/l) and smaller variations at out flow (from 43 to 95 mg/l). The highest reduction of BOD_5 values was obtained at hydraulic load 10 l/min (September), with efficiency 85%. Efficiency of reduction for BOD_5 values range from 32 to 85 %. Average reduction of BOD_5 values was 57 % (figure 29).

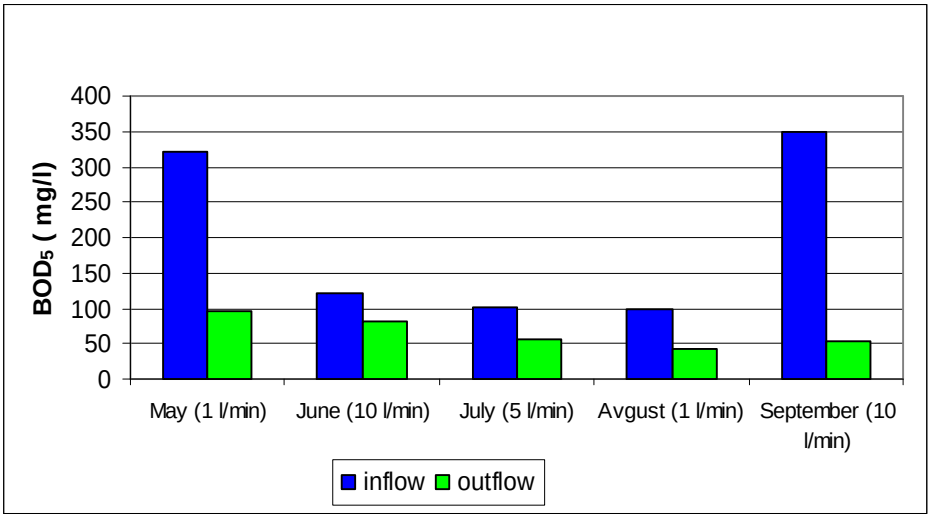

Figure 28: *Result of BOD5 values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 .*

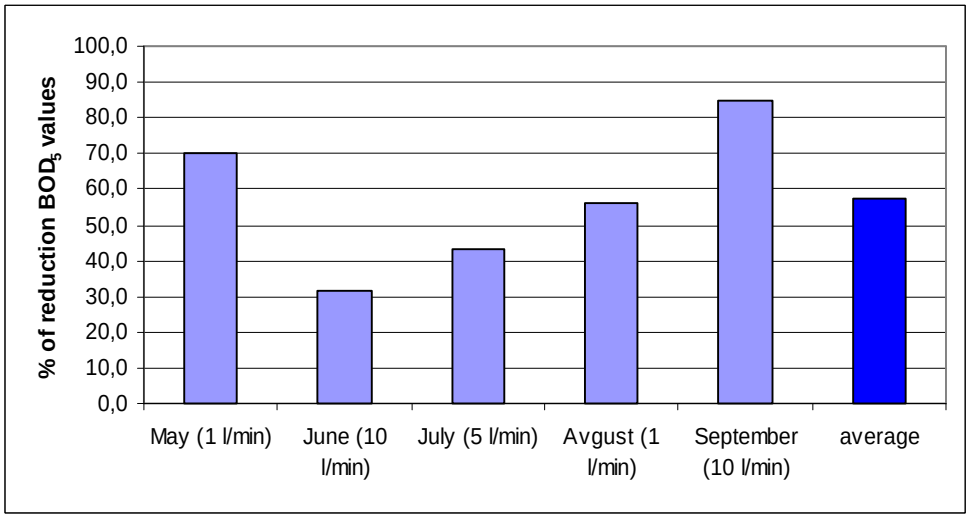

Figure 29: *Result of BOD5 values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figures 30,31 show COD values with large variations at inflow (from 276 to 1379 mg/l) and smaller variations at out flow (from 93 to 153 mg/l). The highest reduction of COD values was obtained at hydraulic load 1 l/min (May), with efficiency 91%. Efficiency of reduction for COD values range from 53 to 91 %. Average reduction of COD values was 77 % (figure 31)

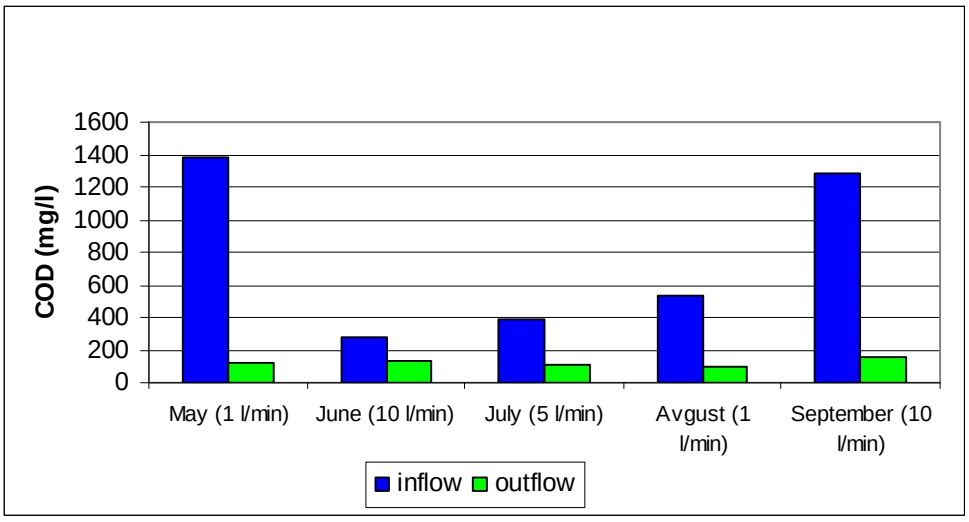

Figure 30: *Results of COD values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005.*

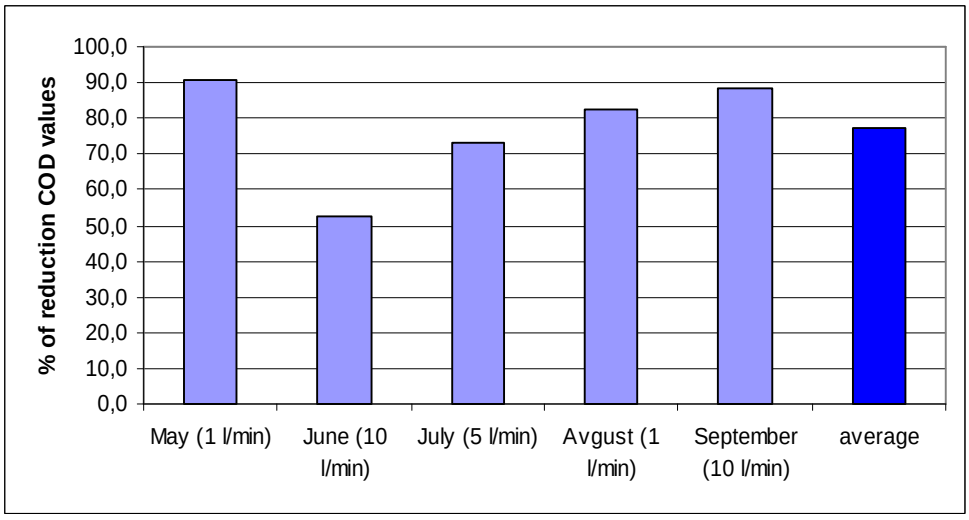

Figure 31: *% of reduction COD values of the waste water at outflow of constructed wetland at different values of hydraulic load during the sampling period May to September 2005 and average of all parameters.*

Figures 32, 33 show TOC values with large variations at inflow (from 74 to 530 mg/l) and smaller variations at out flow (from 15 to 50 mg/l). The highest reduction of TOC values was obtained at hydraulic load 1 l/min (May), with efficiency 95%. Efficiency of reduction for TOC values range from 68 to 95 %. Average reduction of TOC values was 84 % (figure 33).

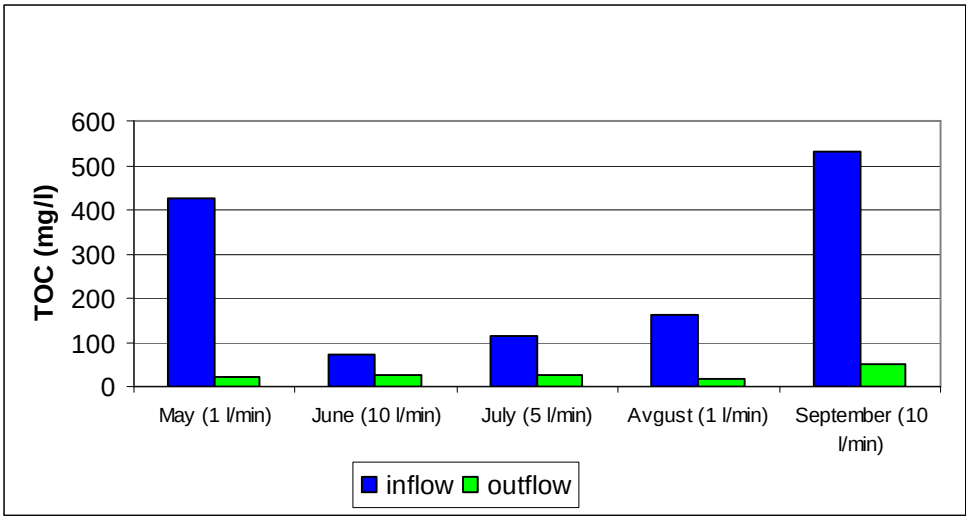

Figure 32: *Result of TOC values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September.*

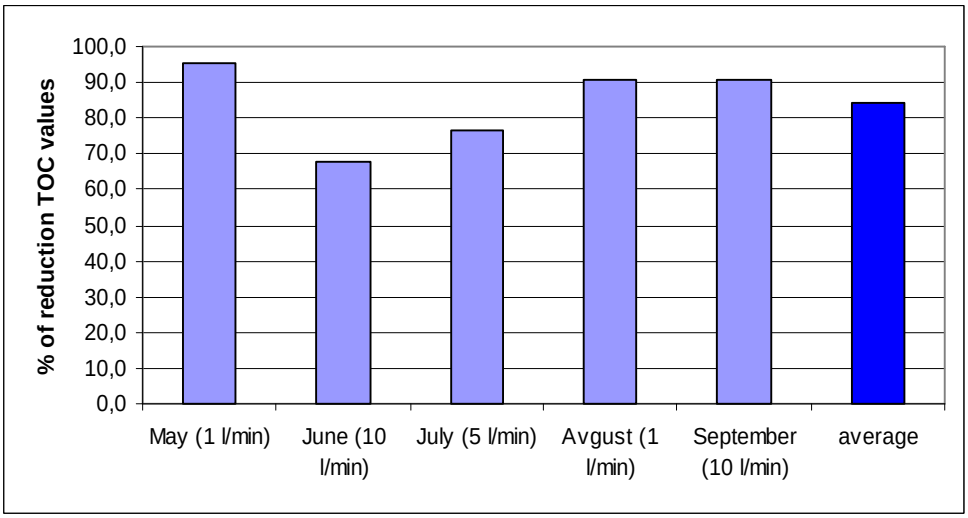

Figure 33: *% of reduction TOC values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figure 34, 35 show AOX values with large variations at inflow (from 30 to 1182 mg/l) and small variations at out flow (from -83 to 95 mg/l). The highest reduction of AOX values was obtained at hydraulic load 5 l/min (July), with efficiency 95%. Results in August (hydraulic load 5 l/min) show growth of AOX at out flow (negative efficiency -83 mg/l). The possible reason for negative values for AOX in August could be experimental error for such a small numbers. Another possible explanation is, that AOX could reminded in beds from July when the values was very high and in August residual AOX from July has been wash out.
Efficiency of reduction for AOX values range from 53 to 95 %. Average reduction of AOX values was 84 %, where negative values from August was excluded (figure 35).

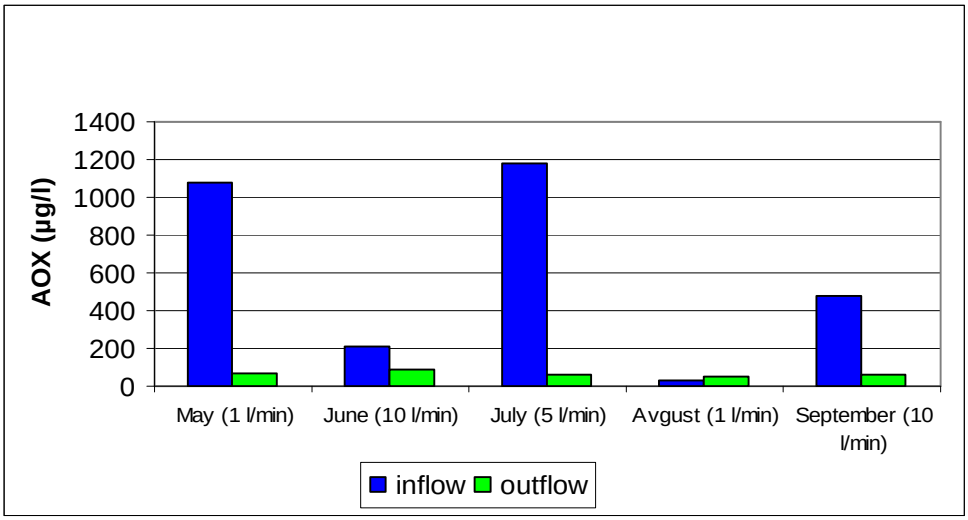

Figure 34: *Result of AOX values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005.*

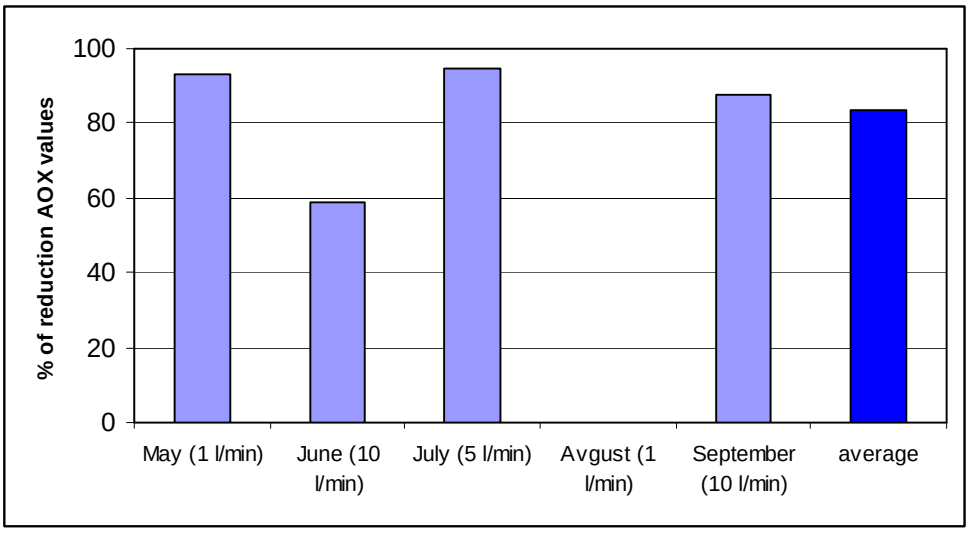

Figure 35: *% of reduction AOX values of the waste water at outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figures 36, 37 show fluctuations in NH_3-N values at inflow (from 0,2 to 4,5 mg/l) and monthly fluctuations at out flow (from 7,05 to 16,05 mg/l). All results show growth of NH_3-N values at outflow. The largest percent increase in NH_3-N values (from 0,2 to 7,05mg/l) was obtained at hydraulic load 1 l/min (August) with negative efficiency of 954%. Average increase of NH_3-N values was 336 %, where values from August was excluded (figure 37).

The possible reason for higher values of NH_3-N at outflow could be connected with higher temperatures in summer months, lower values of oxygen and dying of bacterial population. Nitrification probably did not appear because of low values of oxygen. Another possible reason for the formation of ammonia is change from aerobic to anaerobic microbiological conditions.

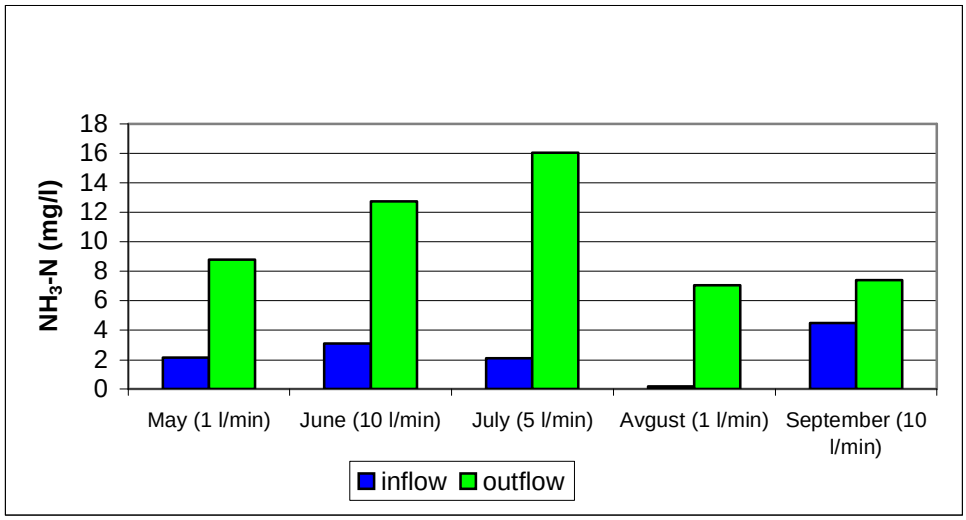

Figure 36: *Result of NH_3-N values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005*

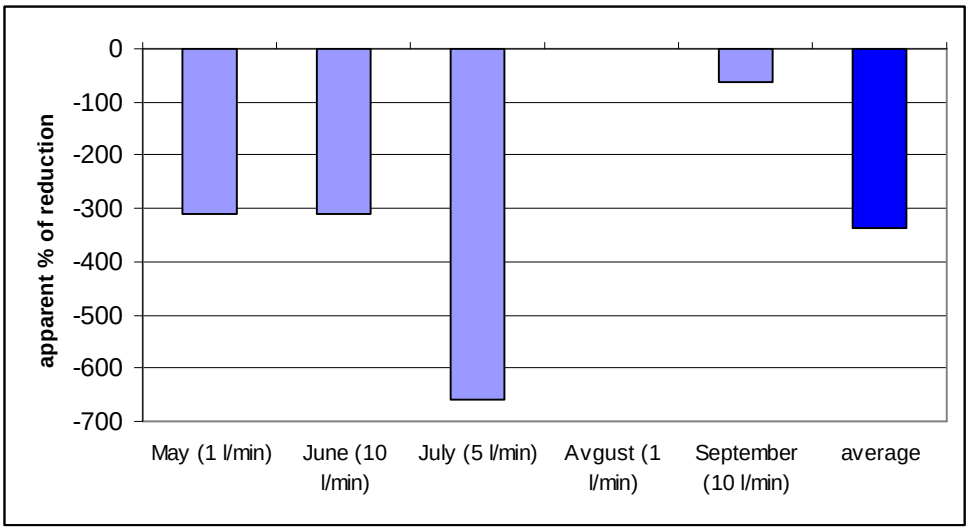

Figure 37: *% of reduction NH_3-N values of the waste water at outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figures 38, 39 show NO_3-N values with large variations at inflow (from 0,11 to 1,0 mg/l) and small variations at out flow (from 0,05 to 0,07 mg/l). The highest reduction of NO_3-N values was obtained at hydraulic load 1 l/min (August), with efficiency 94%. Efficiency of reduction for NO_3-N values range from 55 to 94 %. Average reduction of NO_3-N values was 84 % (figure 39). The possible reason for good efficiency of reduction of NO_3-N values is due to facultative anaerobes (usually bacterium) that could in absence of oxygen use nitrate and nitrite.

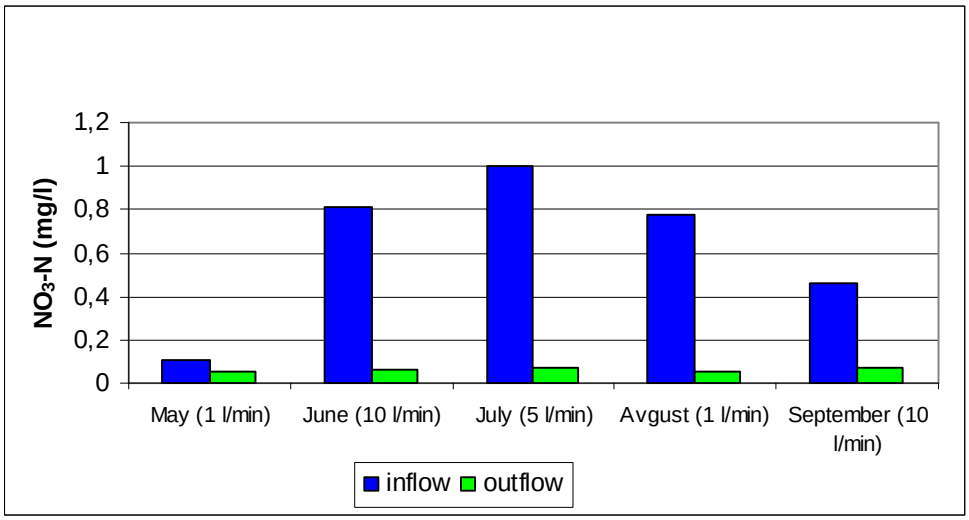

Figure 38: *Result of NO_3-N values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005*

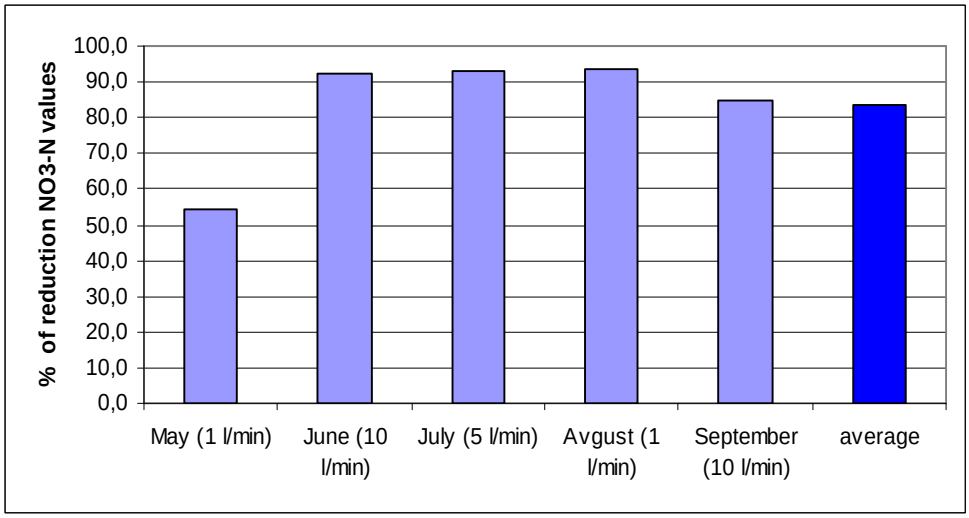

Figure 39: *% of reduction NO_3-N values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figures 40, 41 show small values of NO_2-N at inflow (from 0,11 to 1,0 mg/l) and even smaller values at out flow (from 0,05 to 0,07 mg/l). The highest reduction of NO_2-N values was obtained at hydraulic load 1 l/min (May) and 10 l/min (September), with efficiency 99% in both trials. Efficiency of reduction for NO_2-N values range from 95 to 99 %. Average reduction of NO_2-N values was very high 97 % (figure 41).

The possible reason for good efficiency of reduction of NO_2-N values are due to facultative anaerobes (usually bacterium) that could in absence of oxygen use nitrate and nitrite.

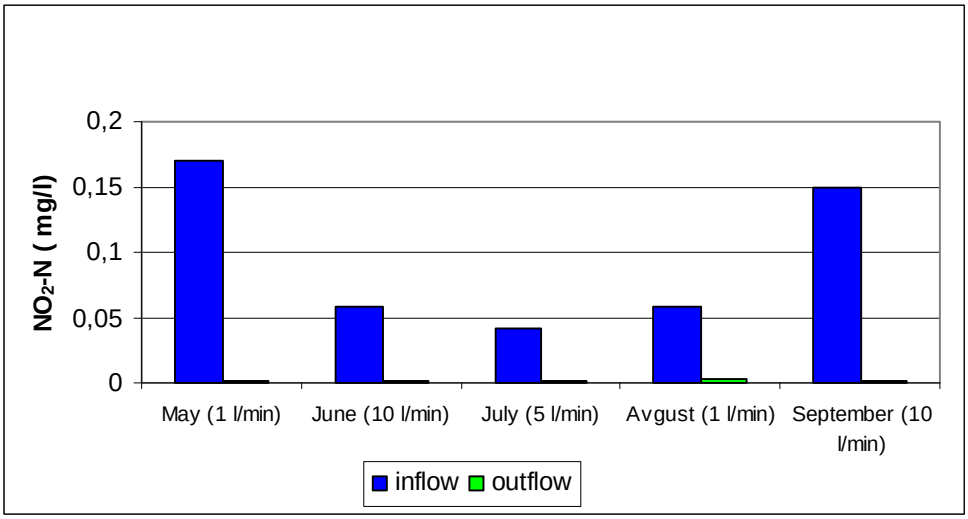

Figure 40: *Result of NO_2-N values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005.*

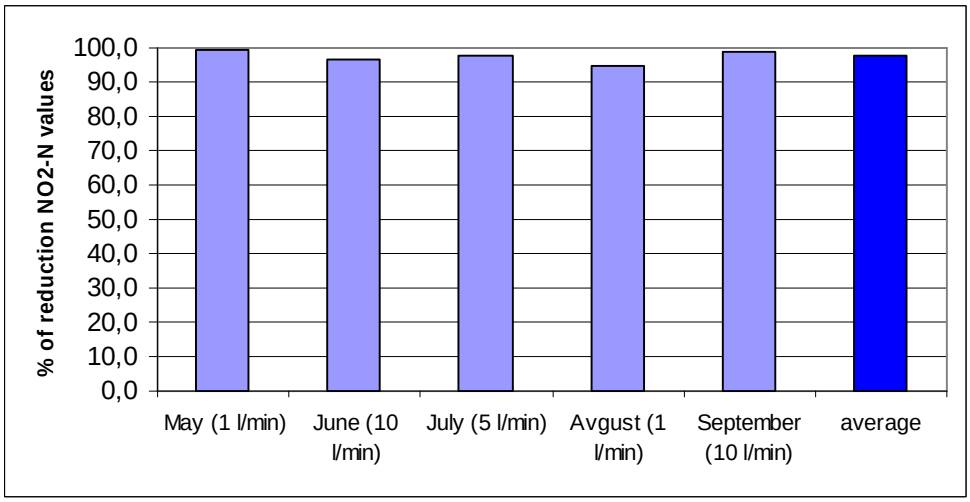

Figure 41: *% of reduction NO_2-N values of the waste water at outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figure 42, 43 show N-total values with large variations at inflow (from 7 to 82,4 mg/l) and smaller variations at out flow (from 10 to 18,7 mg/l). The highest reduction N-total values was obtained at hydraulic load 10 l/min (September), with efficiency 81%. Results in June, July and August show an increase of N-total values at out flow with which results in a negative efficiency. Because of negative efficiency in three sampling the average reduction of N-total values was only 5 % (figure 43).
The possible explanation for higher value of total N at outflow (June, July, August) are due to experimental error for smaller numbers in June, July and August.

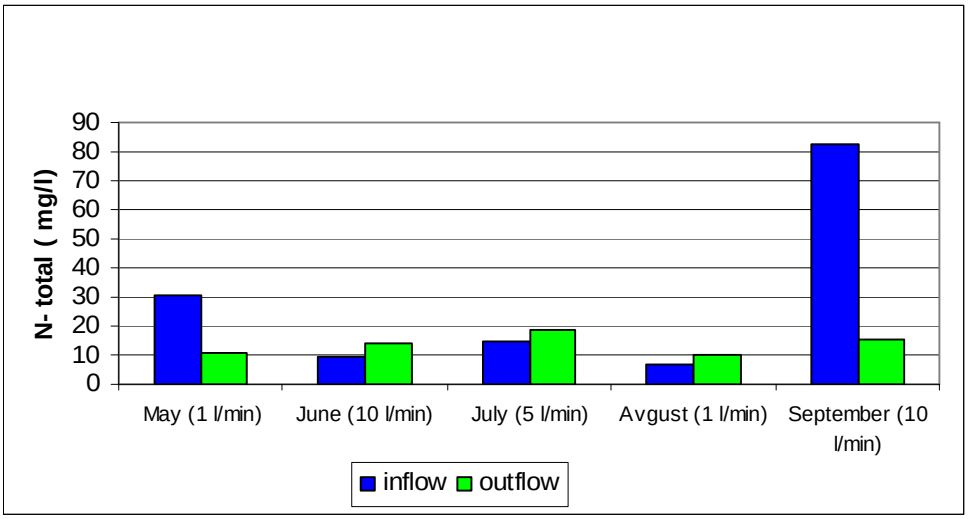

Figure 42: *Result of N- total values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005*

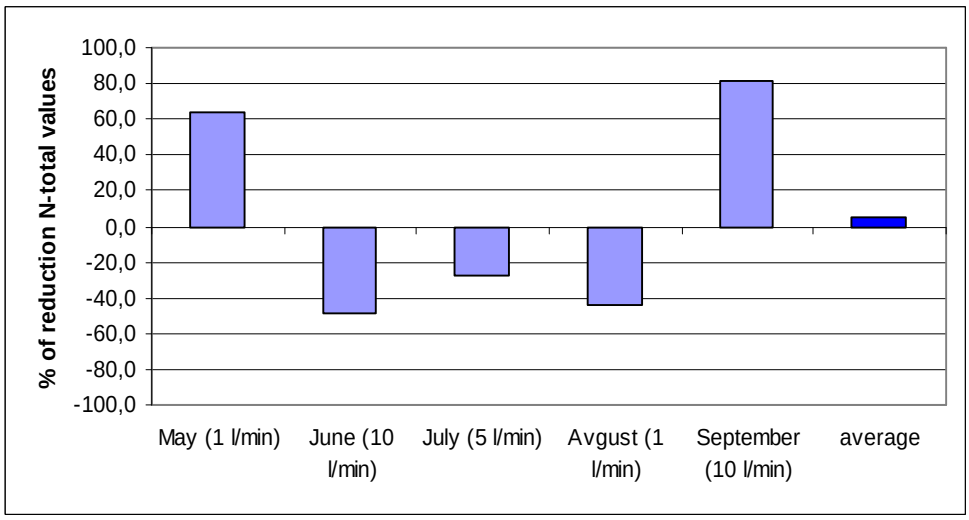

Figure 43: *% of reduction N- total values of the waste water at outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figures 44, 45 show very low P-total values at inflow (from 1,2 to 4,3 mg/l) and also at out flow (from 0,3 to 2,2 g/l). The highest reduction of P-total values was obtained at hydraulic load 1 l/min (June), with efficiency 94%. Result in July (hydraulic load 5 l/min) show an increase of P-total values at out flow (negative efficiency -84 mg/l). Efficiency of reduction for P-total values range from -84 to 94 %. Average reduction of P-total values was 60 %, where negative values from July was excluded (figure 45).
The possible reason for higher values of P- total at out flow in July could be related to the establishment of emergent vegetation and the resulting accumulation of organic sediment which could washing out in July. The another possible reason for negative efficiency for P-total in July could be experimental error for a smaller number in July.

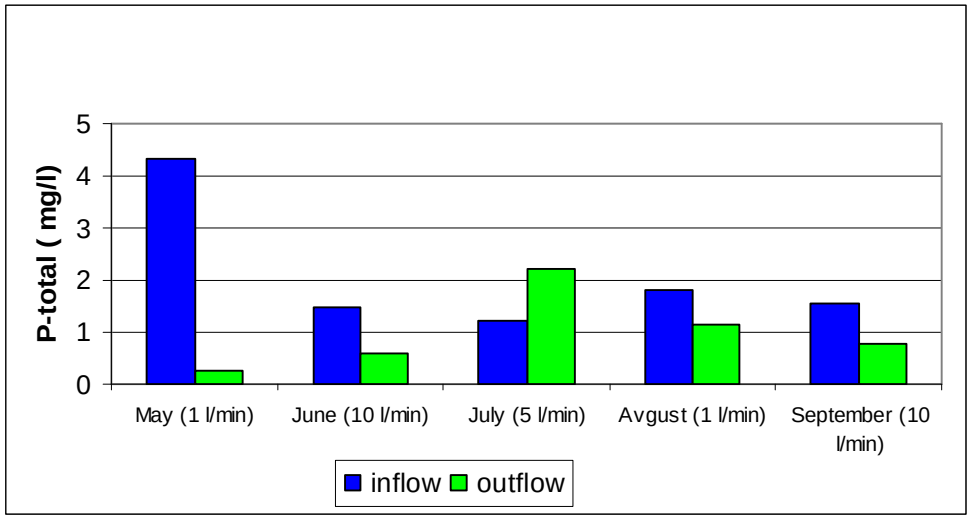

Figure 44: *Result of P- total values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005*

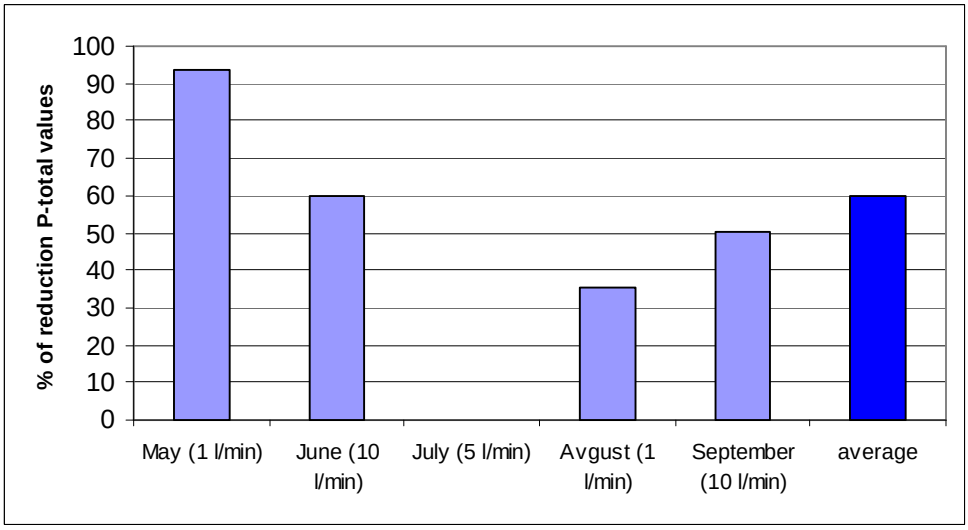

Figure 45: *Result of P- total values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September and average of all parameters.*

Figures 46, 47 show high SO_4 values at inflow (from 76 to 1891 mg/l) and reduced values at out flow (from 75 to 251 mg/l). The highest reduction of SO_4 values was obtained at hydraulic load 10 l/min (June and September) with efficiency 87%. Results in May (hydraulic load 1l/min) show apparent growth of SO_4 values at out flow (resulting in an apparent negative efficiency -46 mg/l). Efficiency for SO_4 values range from -46 to 87 %. Average reduction of SO_4 values was 85,6 % (figure 47), where negative values from May was excluded.
The possible reason for negative SO_4 values in May could be experimental error for such a small numbers, whish appears only this month.

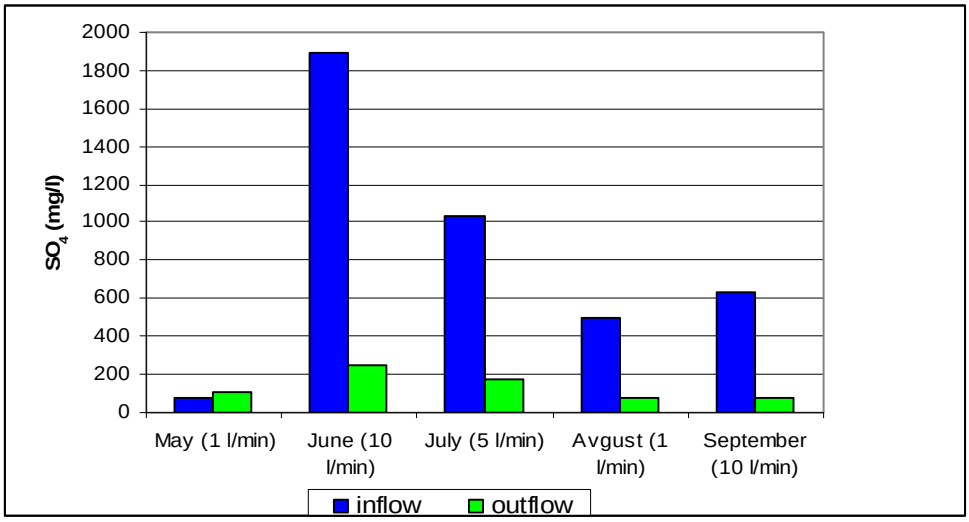

Figure 46: *Result of SO_4 values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005*

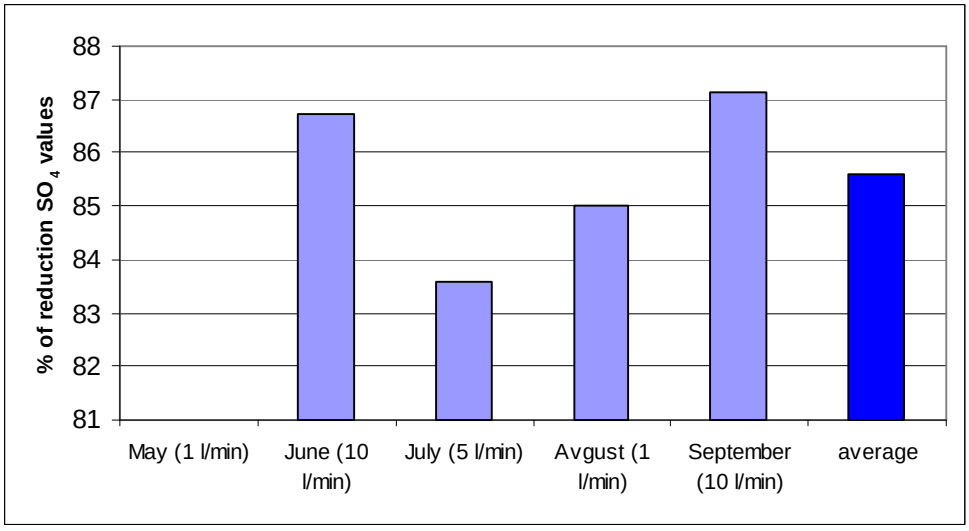

Figure 47: *% of reduction SO_4 values of the waste water at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figure 48 show Spectral Absorption Coefficient (SAC) values at wavelength 436 nm at inflow (from 5 to 34 m^{-1}) and SAC at out flow (from 0 to 4 m^{-1}). The highest decolouration was obtained at hydraulic load 5 l/min (July) with efficiency 99%. Decolouration efficiency ranged from 40 to 99 %. Average decolouration was 80 % (figure 49).
The red line show limit (SAC = 7 m^{-1}) which is regulated as maximum allowed concentration for discharge into water. In most sampling the inflow values of waste water exceeded maximum allowed concentration for discharge into water.

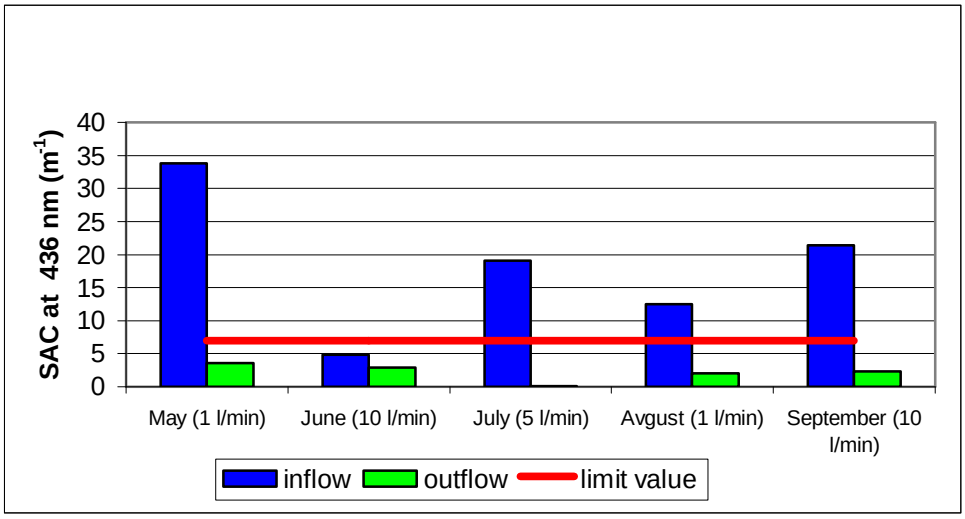

Figure 48: *Results of SAC values of wastewater at wavelength 436 nm at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005.*

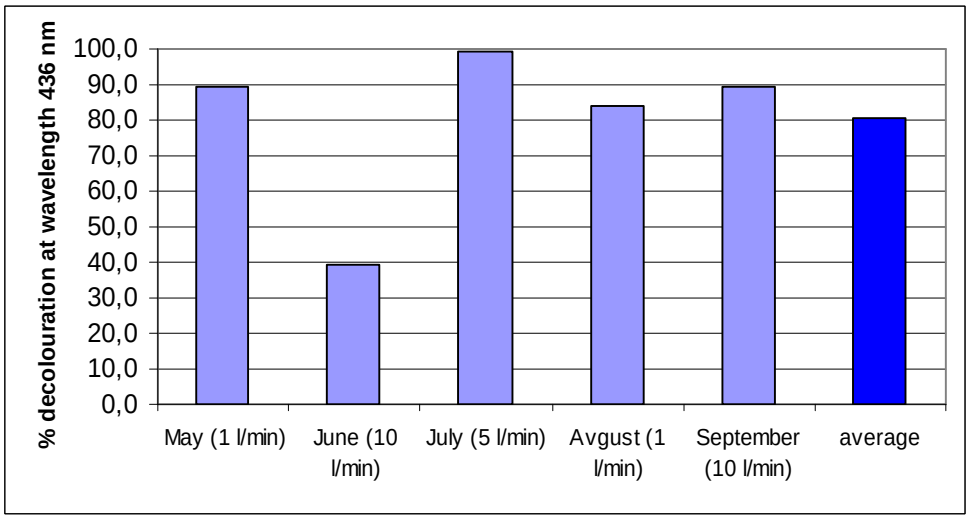

Figure 49: *% of decolouration of wastewater at wavelength 436 nm at outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figure 50 show Spectral Absorption Coefficient (SAC) values at wavelength 525 nm at inflow (from 8,9 to 100 m^{-1}) and SAC at out flow (from 0,8 to 4,5 m^{-1}). The highest decolouration was obtained at hydraulic load 1 l/min (May) with efficiency 96%. Decolouration efficiency ranged from 71 to 96 %. Average decolouration was 89 % (figure 51). The red line show limit (SAC = 5 m^{-1}) which is regulated through the legislation as required maximum concentration for discharge into water. In all sampling the inflow values of waste water exceeded require concentration for discharge into water.

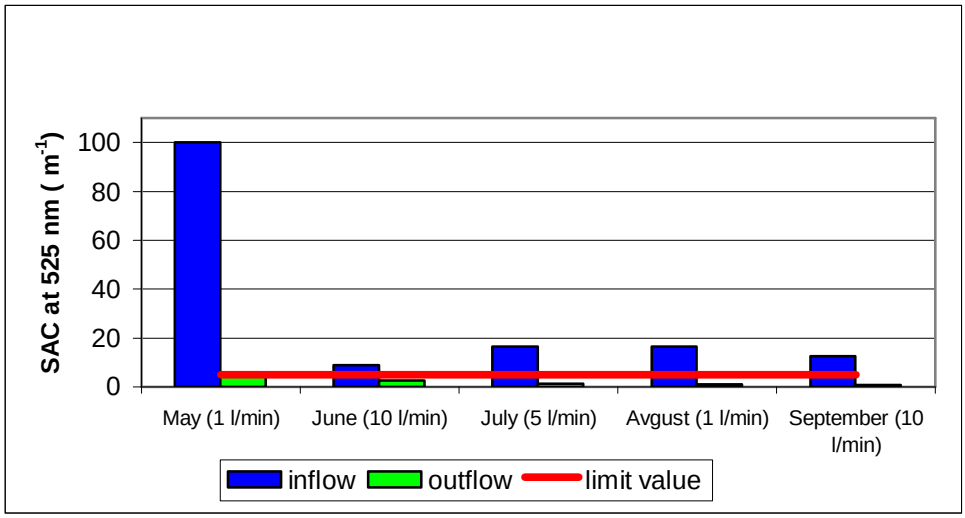

Figure 50: *Result of SAC values of wastewater at wavelength 525 nm at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005..*

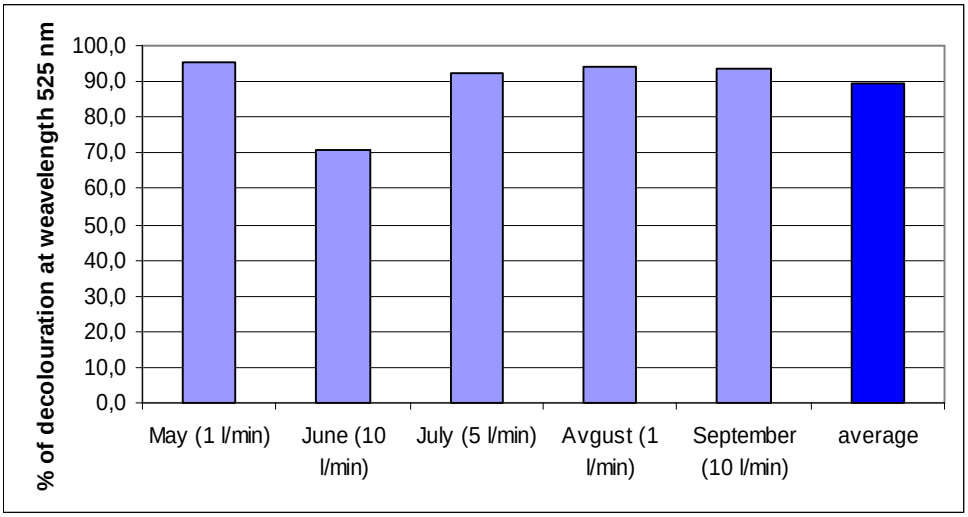

Figure 51: *% of decolouration of wastewater at wavelength 525 nm at outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

Figure 52 show Spectral Absorption Coefficient (SAC) values at wavelength 620 nm at inflow (from 4,5 to 16,3 m^{-1}) and SAC at out flow (from 0,4 to 1,3 m^{-1}). The highest decolouration was obtained at hydraulic load 5 l/min (July) with efficiency 95%. Decolouration efficiency ranged from 75 to 95 %. Average decolouration was 86 % (figure 53)
The red line show limit (SAC = 3 m^{-1}) which is regulated as required maximum concentration for discharge into water. In all sampling the inflow values of waste water exceeded required maximum concentration for discharge into water.

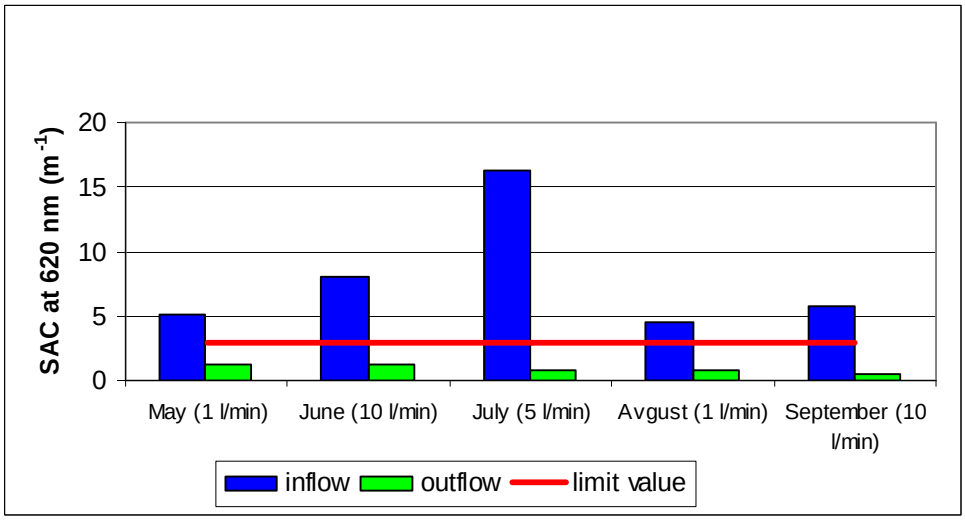

Figure 52: *Results of SAC values of wastewater at wavelength 620 nm at inflow and outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005.*

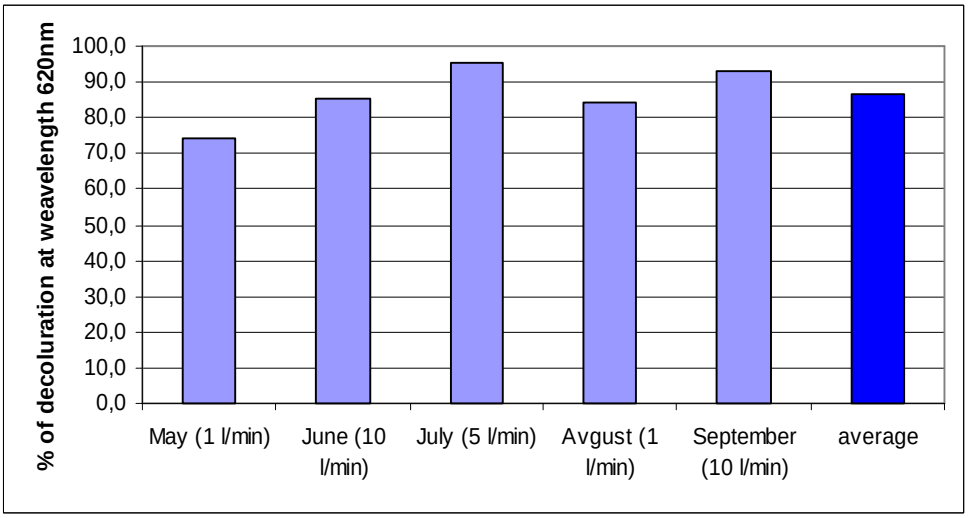

Figure 53: *% of decolouration of wastewater at wavelength 620 nm at outflow of constructed wetland at different values of hydraulic load in sampling period May to September 2005 and average of all parameters.*

6. 3. Results of decolouration of wastewater with thermo/UV/hydrogen peroxide process

The results shown in the figure 54-56 present decolouration (value of absorbance) of textile waste water at three wavelength (436 nm, 525 nm, 620 nm) in seven different time of sampling of wastewater from the company Tekstina. Results show that after decolouration with thermo/ UV/hydrogen process the values of absorbance were zero or approximately zero after time period 45-100 min. The average time of decolouration was 76 min, the minimum time of decolouration was 45 min (wastewater sampling on 30.05.05), the maximum time of decolouration was 100 min (wastewater sampling on 27.06.05). Duration of thermal part was 60 min and is separated from UV part with vertical arrow in figures 54, 55 and 56.

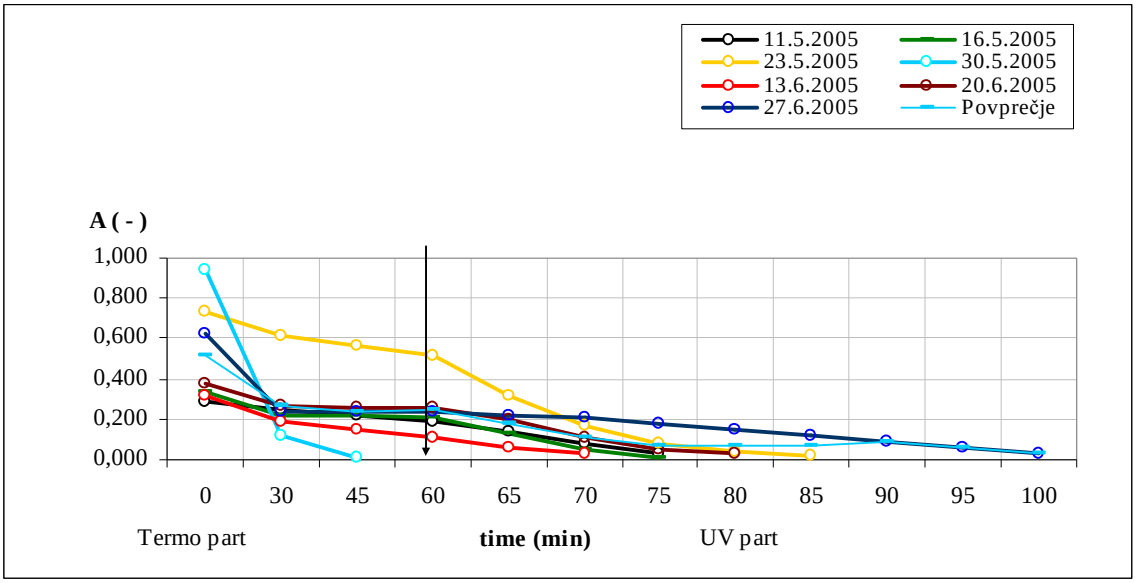

Figure 54: *Results of wastewater decolouration with thermo/UV/hydrogen peroxide process at wavelength 436 nm, sampling period May to June 2005*

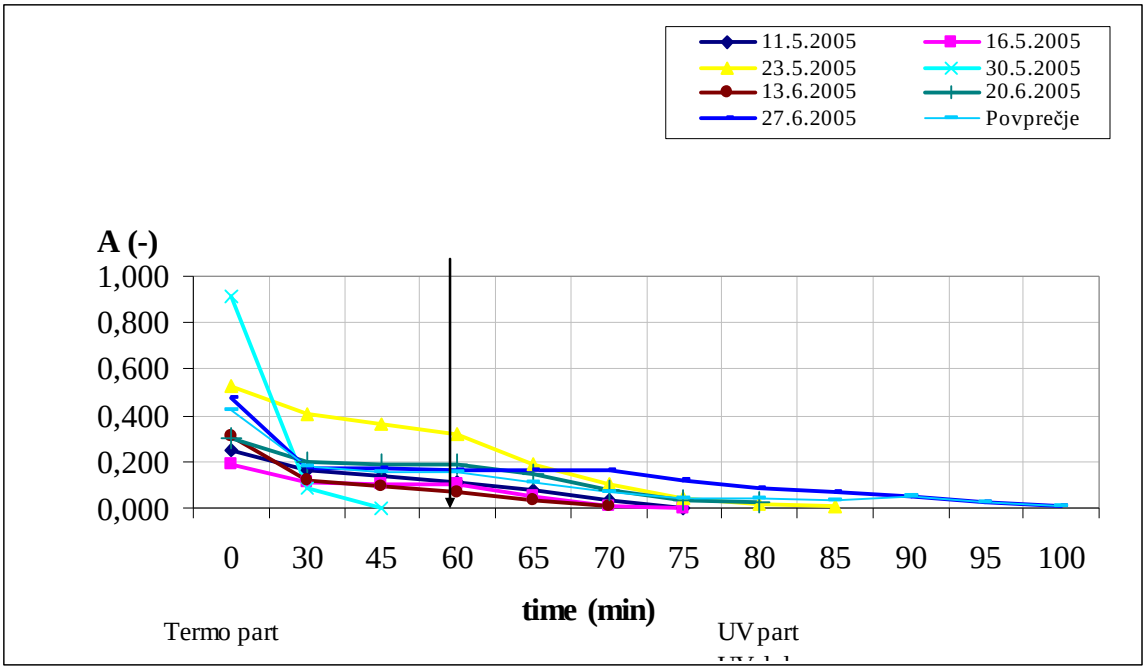

Figure 55: *Results of wastewater decolouration with thermo/UV/hydrogen peroxide process at wavelength 525 nm, sampling period May to June 2005*

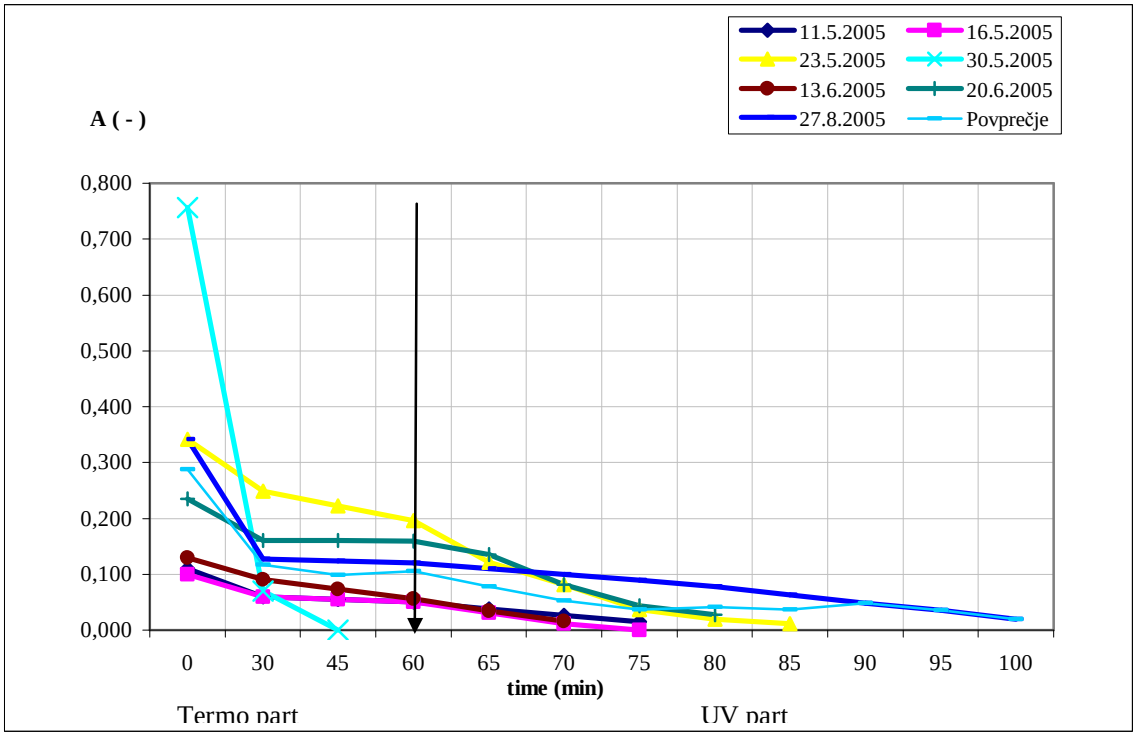

Figure 56: *Results of wastewater decolouration with thermo/UV/hydrogen peroxide process at wavelength 620 nm, sampling period May to June 2005*

The results obtained in the figure 57-59 present comparison of % decolouration between thermo and UV part at three wavelength (436 nm, 525 nm, 620nm) in seven different time of sampling of wastewater in sampling period May to June 2005. The minimum % of decolouration in thermo part was obtained at wastewater sampling on 20.06.05, the maximum % of decolouration in thermal part was obtained at wastewater sampling on 30.05.05, where decolouration of wastewater was 100 % completed already in thermal part.

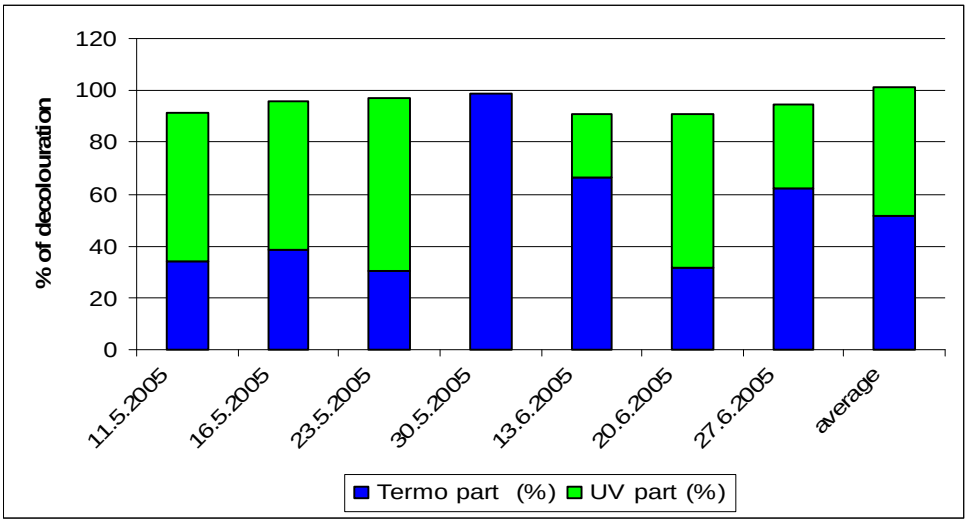

Figure 57: *Comparison of wastewater decolouration between thermo an UV part at wavelength 436 nm and average of all parameters, sampling period May to June 2005*

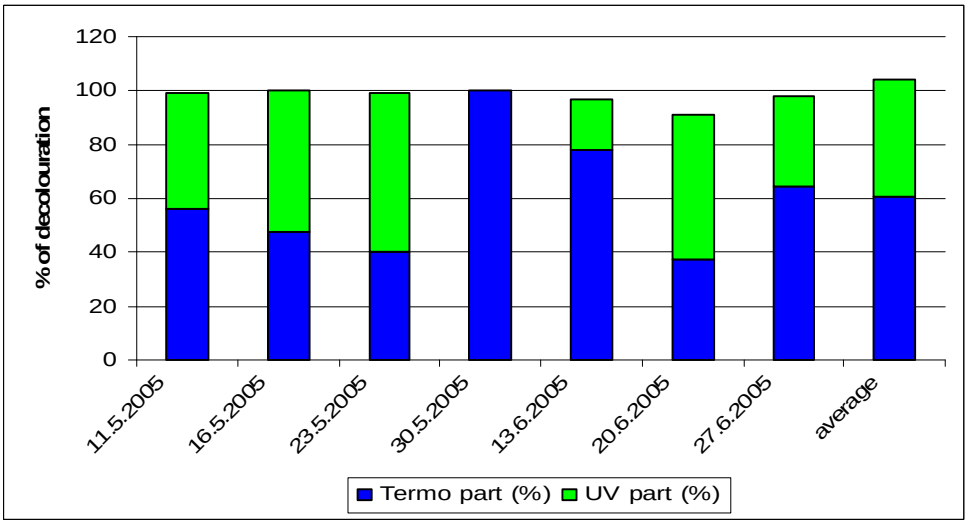

Figure 58: *Comparison of wastewater decolouration between thermo an UV part at wavelength 525 nm and average of all parameters, sampling period May to June 2005*

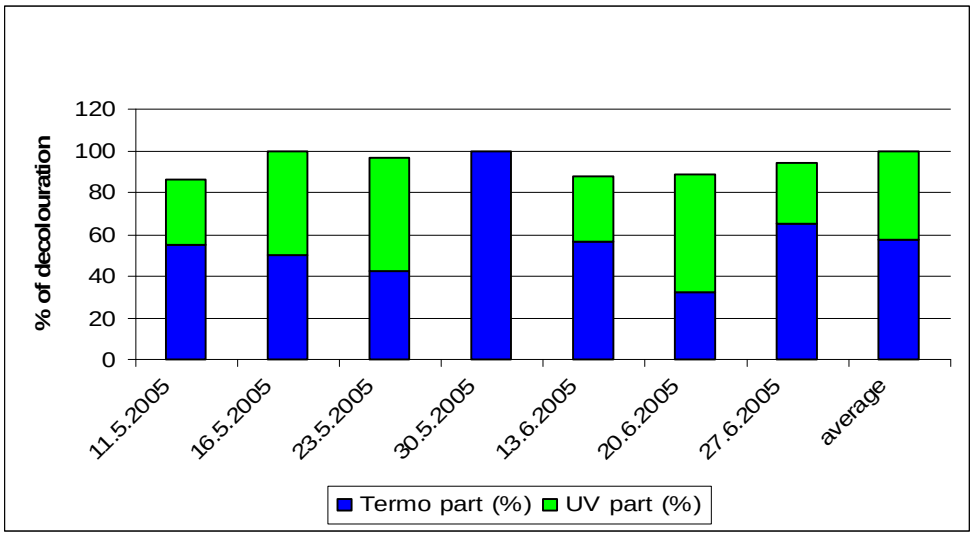

Figure 59: *Comparison of wastewater decolouration between thermo and UV part at wavelength 620 nm and average of all parameters, sampling period May to June 2005*

The results in figure 60 present TOC values before decolouration and after thermo and UV part of decolouration in seven different time of sampling of textile waste water. With thermo/UV hydrogen peroxide process, TOC values were reduced in the average from 153,3 mg/l (before decolouration) to 56,4 g/ml (after thermo/UV part).

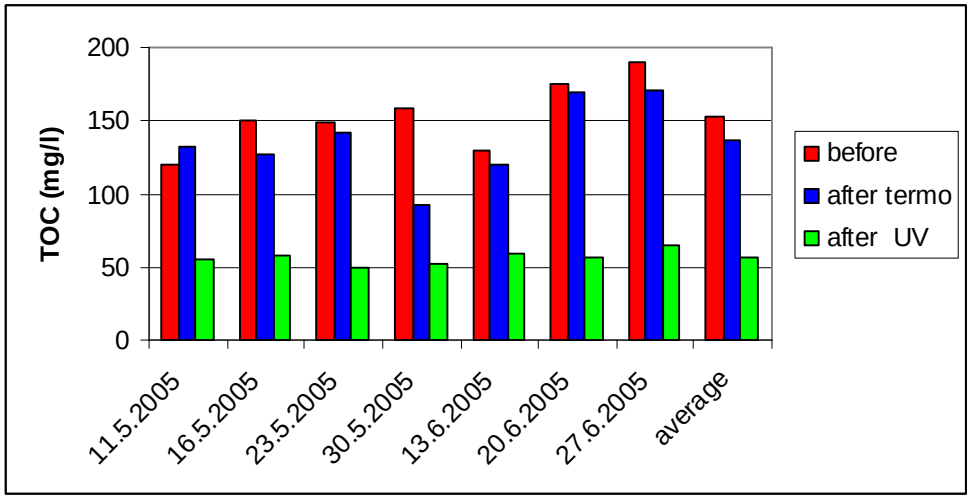

Figure 60: *Results of TOC values before and after decolouration with thermo and UV part and average of all parameters, sampling period May to June 2005*

The results in figure 61 show % of TOC reduction after thermo/UV part in seven different time of sampling of textile waste water. The minimum reduction of TOC values was 54,3% (wastewater sampling on 11.05.05), and the maximum reduction of TOC values was 67,7% (wastewater sampling on 20.06.05). The average reduction of TOC values was 62,5%.

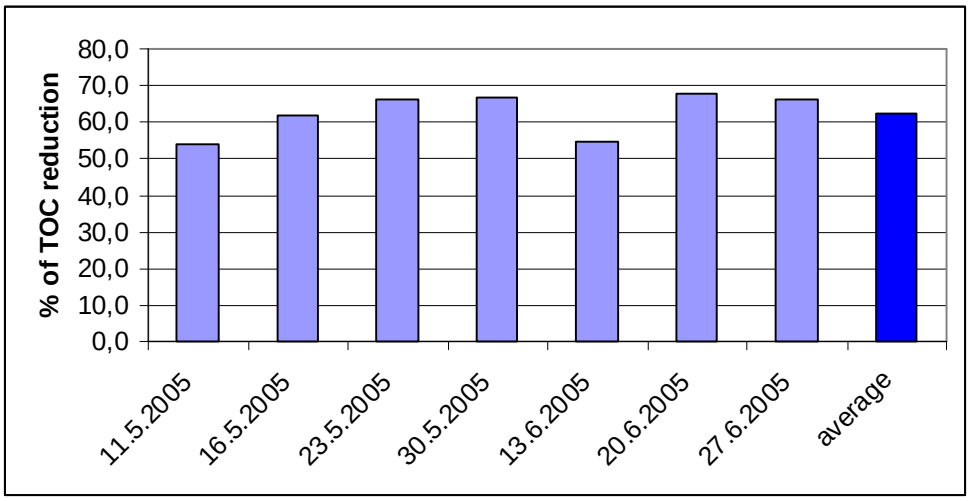

Figure 61: *% of TOC reduction after decolouration(with thermo/UVpart) and average of all parameters, sampling period May to June 2005*

7. ECONOMICAL EVALUATION

On the basis of the results obtained, some economic consideration can be drawn to foresee the economical feasibility of the implementation of the investigated cleaning techniques for the treatment of textile effluent from the company Tekstina d.d. Cleaning technique with hydrogen peroxide/ UV is not yet available for production use and for this, reason the economical evaluation was not done**.**

7. 1. Economic analysis for reverse osmosis plant

The RO plant is planed for the approximate wastewater capacity of 290 000 m^3. It would be divided into two lines of 20 m^3/h each which could be used in parallel or individually as dictated by the daily waste water treatment needs. Both lines would be designed for automated use. A manually operated membrane cleaning system for this operation is required. The RO plant has to be limited to a maximum recovery of 88%. This are the recommendation of producer of RO plant Aquious-PCI Membranes. For textile industry RO membranes, usually require the use of a prefiltration stage. In this case sand filtration was employed to avoid ingress of textile fibres into the system which would have otherwise resulted in the flow channel being obstructed.
In the table17 is presented specification of RO plant.

Table 17 *Specification of RO plant*

Feed volume	40m^3/h
Permeate volume	35m^3/h
Operating time	24 hours/day
Floor space requirements	8m x 1,5 m x 2m high

In the table 18 are presented investment costs (evaluated in EUR) for RO plant in comparison with the total water cost for year 2004 for the company Tekstina.

Table 18 *Investment cost of RO plant and total water cost for year 2004 for company Tekstina*

Class of costs	**(EUR)**
Investment cost of RO plant	210.000,00
Yearly membrane costs	36.000,00
Total water cost for year 2004	270.639,55

Figure 62 shows classification of water cost in % for company Tekstina d.d. where the main cost (75,5%) is cost for wastewater treatment.

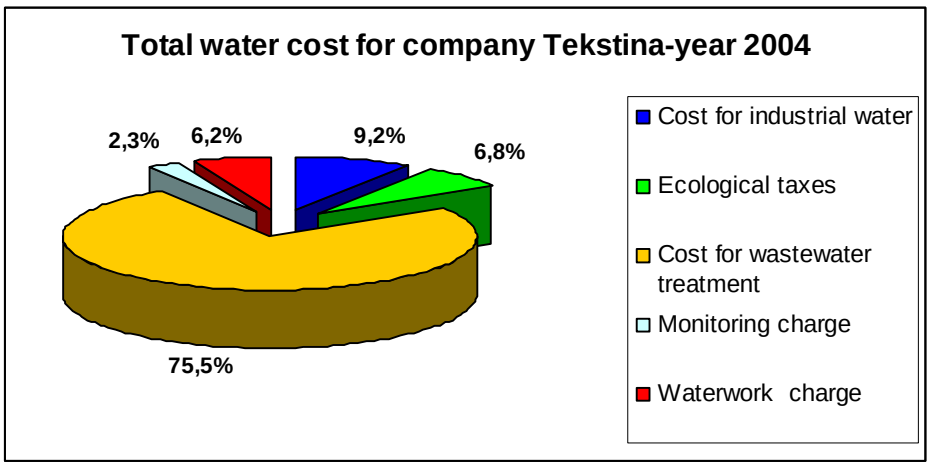

Figure 62: *Classification of water cost in % for company Tekstina for the year 2004*

With RO plant Tekstina could treat the wastewater on site (or in house). Total water cost would be dramatically reduced, and simultaneously, present and future environmental legislation would be met. The permeate produced by RO can be reused for all the technological uses. The reuse of hot water would imply significant energy saving. Concentrate produced (present 10-12% of wastewater) with RO could be filtered and the sludge produced could be disposed to nearest landfill. The chemical analysis of present sludge show that is classified as non-hazardous waste.

7. 2. Economic analysis for Constructed Wetland plant

Constructed wetland purifying belongs to a group of alternative methods, most commonly combined with other methods (e.g. flocculation/coagulation) as the final step in wastewater treatment. However in this work CW was optimized and then used as the only treatment to purify wastewater from company Tekstina. Required area will be 11.349 m^2 (with 0,3 porosity of substrate and depth 0,7m). Consideration of the required area being too big, lead to conclusion that also 50% efficiency would be acceptable with holding time 11 hours in the combination with other cleaning technique. In this case required area will be 2400 m^2. In the table 19 are presented costs for CW construction:

Table 19 *Construction cost for CW*

Class of cost	**EUR**
Outline scheme cost	3.547,88
PGZ-PZI cost	5.008,77
Maintenance cost	300,53
Construction cost	225.394,63
Total Cost	**234.251,81**

Because the use of CW did not satisfied the purification requirements for water reuse, additional purifying has to be carried out.

8. DISCUSION

8. 1. Method with reverse osmosis

As the results of pilot experiments it was found that RO is effective for filtration of textile effluent. It gives very high quality of water for all measured parameters. The RO permeate had good analytical characteristics: the COD values was reduced by 98%, BOD_5 by 99%, sulphates by 99%, the SAC values at wavelength 436 nm by 97% , the SAC values at wavelength 525 nm by 98%, the SAC values at wavelength 620 nm by 86%. The average purification was 96%. According to the small testing trials further experiments has to be done for the optimal selection of membrane system.
Because of very good results the permeate could be reuse for all technological use. Further more the reuse of hot water would imply significant energy saving.
The problem to be consider was the tiny fibrous material, mainly cotton fibres, washed down from the production process. This fibrous material has the tendency to accumulate in the membrane system. Therefore the prefiltration unit has to be applied. Concentrate produced during water purifying is classified as non-hazardous waste and could be disposed to landfill .

PCI –Memtech reported that a number of textile companies have evaluated water recovery and reuse, and in general the payback time range from a little under two years to four years.
In consideration of good results obtained, some economical consideration can be drawn to evaluate the economical feasibility of the implementation of membrane processes on the industrial scale.

8. 2. Method with constructed wetland

Experiments on constructed wetland in general show high efficiency for the measured parameters of textile waste water. The CW had following average analytical characteristics: the values of suspended solids was reduced by 83%, COD by 77%, BOD_5 by 57%,NH_3-N show negative efficiency by -336%, NO_3-N by 84%, NO_2-N by 97%, N-total by 5%, P total by 60%, the SAC values at wavelength 436 nm by 80% , the SAC values at wavelength 525 nm by 89%, the SAC values at wavelength 620 nm by 86%, sulphates by 86%, AOX by 84, TOC by 84%. In the most cases, the highest efficiency was obtained with hydraulic load 1 l/min. The average purification was 75%. In the calculation of the average the negative values were excluded. Decolouration with CW is very good but not sufficient for water reuse for all technological use in textile process and additional cleaning technologies are required.
The main disadvantage of CW is too big required area 11350 m^2 for the company Tekstina, with hydraulic load 1100 m^3/day and with a wastewater holding time of 52 hours.

8. 3. Method with thermo/UV/hydrogen peroxide process

The efficiency of decolouration textile wastewater with thermo/UV/hydrogen peroxide process was examined by time-dependent colour intensity reduction at three wavelength and by determining ecological parameter TOC. The average time of decolouration was 76 min, the minimum time of decolouration was 45 min, the maximum time of decolouration was 100 min.
The minimum reduction of TOC values was 54,3%, the maximum reduction of TOC values was 67,7% and the average reduction of TOC values was 62,5%.
It was found that this method show good decolouration in short reaction time with no sludge and no salts formation during water purifying. For this method I was not find available technology for industrial use.

8. 4. Advantages and disadvantages of investigated methods

The advantages and disadvantages of the methods investigated are tabulated below.

Table 20 *Advantages and disadvantages of investigated methods*

Method with RO	
Advantages	**Disadvantages**
very high quality of water	prefiltration unit for fibre (sand filters)
water reuse for technological use	high membrane costs
water recycling	concentrate disposal
energy saving	
Method with CW	
Advantages	**Disadvantages**
relatively cheap to build and operate	not sufficient decolouration
easy to maintain	additional method to meet legislation requirements
synergy with environment	not economical considerable for textile industry
	large space
Method with thermo /UV/ H_2O_2	
Advantages	**Disadvantages**
good decolouration results	not available technology for industrial use
no sludge formation	not applicable for all dye types
no salt formation	required separation of suspended solid particles
short reaction time	

9. CONCLUSION

The following conclusions were drawn from this thesis research:

- The use of membrane technology (RO) has been very effective for purification of textile wastewater and meeting regulatory standards for discharge into water. The overall removal efficiency of COD, BOD_5, sulphates and colour were found to be 96%. Almost complete colour removal was achieved with RO. The permeate produced by RO can be reused in the technological process. Furthermore the reuse of hot water would imply significant energy saving. According to high taxes for water and wastewater cleaning additional saving would be realized from the discharge of smaller volumes of wastewater to wastewater treatment plant.

- The economic analyses shows the benefits of implementing RO technology at the company Tekstina. However, correctly applied, membrane filtration could provide financial saving conserve resources and help meet environmental legislation. Further research is necessary for implementation membrane technology for waste management in company Tekstina. It is important to carry out extensive trials on pilot scale in the production to ensure the membrane technology will be compatible with application.

- Results of constructed wetland (CW) pilot plant show that variable textile influent and as well as the hydraulic load has great influence on efficiency of the system. Decolouration of wastewater as a main parameter was in average 85%. Because the use of CW did not lead to complete decolouration (approximately 15 % of dyestuff resides in wastewater), additional purifying has to be carried out in order to obtain the limits regulated through legislation. Constructed wetland (CW) show 75% efficiency of measured parameters (suspended solids, COD, BOD5, NO_3-N, NO_2-N, N-total, P-total, SO_4^{2-} values, decolouration at wavelength 436 nm, 525 nm, 620 nm) which is much lower than RO.

- Implementation of CW is not economical considerable especially because other cleaning technique will be necessary and also required area is too big.

- The decolourisation of textile effluent under thermo/UV/hydrogen peroxide process was found as suitable. The study has shown that the efficiency of decolouration in thermal part was 56% in average time 60 minutes. Decolouration was enhanced by the residual thermal energy in the waste water from dying process. No additional heating was necessary. In UV part, the decolouration of the residual 44 % occurred in average time 23 minutes. The study also determined reduction of TOC values with efficiency of 62,5% (from 153,1 mg/l to 56,4 mg/l). The TOC values was under the limits set by Slovenian regulation (30 mg/l) for discharge into water.

- Method with thermo/UV/hydrogen peroxide is not yet available for production use and economical evaluation was not done.

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APPENDIX

EXPERIMENT I – Results of decolouration of wastewater with process of Reverse osmosis(RO)

Table 1.1: Parameters of the wastewater quality at inflow and outflow of RO pilot plant

Parameter	Sampling point 1		Efficency %
	wastewater	Permeate	
pH	9,19	7,31	/
COD (mg O_2/l)	536	9	98
BOD_5 (mg O_2/l)	139	1	99
Sulphates (mg/l)	245	2,9	99
Colour 436 nm (m^{-1})	6,18	0,18	97
Colour 525 nm (m^{-1})	17,76	0,32	98
Colour 620 nm (m^{-1})	1,81	0,25	86
Average			96

Table1.2. : Result of wastewater decolouration(SAC Values) at three wavelength (436 nm, 520 nm, 620 nm at inflow and outflow with limit values required for discharge into water and % of efficiency

average- SAC	wastewater (m^{-1})	permeat (m^{-1})	limit-SAC	Efficiency (%)
Colour 436	6,18	0,18	7	97
Colour 525	17,76	0,32	5	98
Colour 620	1,81	0,25	3	86

EXPERIMENT II - Results of decolouration of wastewater with biological purification of wastewaters with helophytes planted in constructed wetland (CW)

Table 2.1: Parameters of the wastewater quality before and after purifying process at different values of hydraulic load in time period of experiment from May 2005 to September 2006

Hydraulic load	May (1 l/min)		June (10 l/min)		July (5 l/min)		August (1 l/min)		September (10 l/min)		Efficiency
Parameter	inflow	outflow	inflow	outflow	inflow	outflow	inflow	outflow	inflow	Outflow	(%)
Susp. solids (mg/l)	408	10	52	7	27	9	30	8	128	11	83
COD (mg/l	1379	127	276	130	389	105	528	93	1282	153	77
BOD_5 (mg/l)	320	95	120	82	101	57,1	98,5	43	350	54	57
NH_3-N (mg/l)	2,15	8,8	3,1	12,72	2,11	16,05	0,2	7,05	4,5	7,41	/
NO_3-N (mg/l)	0,11	0,05	0,81	0,06	1	0,07	0,78	0,05	0,46	0,07	84
NO_2-N (mg/l)	0,17	0,001	0,058	0,002	0,042	0,001	0,058	0,003	0,15	0,002	97
N-total (mg/l)	30,45	10,88	9,56	14,25	14,63	18,69	6,99	10,04	82,39	15,46	5
P-total (mg/l)	4,32	0,27	1,5	0,6	1,21	2,23	1,8	1,16	1,57	0,78	31
SAC at 436 nm	33,8	3,6	4,8	2,9	19,1	0,1	12,5	2	21,4	2,3	80
SAC at 525 nm	100	4,5	8,9	2,6	16,6	1,3	16,6	1	12,6	0,8	89
SAC at 620 nm	5,1	1,3	8,1	1,2	16,3	0,8	4,5	0,7	5,8	0,4	86
SO_4 (mg/l)	75,5	110	1891	251	1030	169	500	75	630	81	59
AOX (µg/l)	1080	74	215	88	1182	62	30	55	480	60	50
TOC (mg/l)	425	21	74	24	115	27	162	15	530	50	84
Average											68

EXPERIMENT III: Results of decolouration of wastewater with thermo/UV/Hydrogen peroxide process

Table 3.1: Results of wastewater decolouration with thermo/UV/hydrogen peroxide process at wavelength 436 nm

Min/date	11.5.05 A (/)	16.5.05 A(/)	23.5.05 A(/)	30.5.05 A(/)	13.6.05 A(/)	20.6.05 A(/)	27.6.05 A(/)	average A(/)
0	0,290	0,340	0,736	0,940	0,321	0,378	0,623	0,518
30	0,250	0,220	0,615	0,114	0,188	0,263	0,240	0,270
45	0,220	0,215	0,563	0,011	0,148	0,261	0,238	0,236
60	0,190	0,210	0,511		0,107	0,258	0,236	0,252
65	0,135	0,130	0,317		0,061	0,198	0,220	0,177
70	0,080	0,050	0,168		0,029	0,110	0,204	0,107
75	0,025	0,014	0,075			0,054	0,174	0,068
80			0,044			0,034	0,144	0,074
85			0,023				0,118	0,070
90							0,091	0,091
95							0,057	0,057
100							0,033	0,033

Table 3.2 : Results of wastewater decolouration with thermo/UV/hydrogen peroxide process at wavelength 525 nm

Min/date	11.5.05 A	16.5.05 A	23.5.05 A	30.5.05 A	13.6.05 A	20.6.05 A	27.6.05 A	average A
0	0,250	0,190	0,529	0,914	0,307	0,304	0,471	0,424
30	0,160	0,110	0,403	0,084	0,124	0,195	0,171	0,178
45	0,135	0,105	0,360	0,000	0,096	0,193	0,169	0,151
60	0,110	0,100	0,316		0,068	0,191	0,167	0,159
65	0,074	0,055	0,189		0,033	0,147	0,164	0,110
70	0,038	0,009	0,101		0,010	0,081	0,161	0,067
75	0,002	0,000	0,041			0,036	0,125	0,041
80			0,021			0,027	0,089	0,046
85			0,005				0,070	0,037
90							0,050	0,050
95							0,024	0,024
100							0,010	0,010

Table 3.3: Results of wastewater decolouration with thermo/UV/hydrogen peroxide process at wavelength 620 nm

Min/date	11.5.05 A	16.5.05 A	23.5. 05 A	30.5. 05 A	13.6. 05 A	20.6. 05 A	27.6. 05 A	average A
0	0,110	0,100	0,341	0,757	0,129	0,235	0,342	0,288
30	0,060	0,060	0,249	0,070	0,091	0,161	0,127	0,117
45	0,055	0,055	0,223	0,000	0,074	0,160	0,124	0,099
60	0,050	0,050	0,196		0,056	0,159	0,120	0,105
65	0,038	0,031	0,122		0,034	0,135	0,110	0,078
70	0,027	0,012	0,081		0,016	0,081	0,100	0,053
75	0,015	0,000	0,037			0,043	0,089	0,037
80			0,019			0,027	0,078	0,041
85			0,011				0,063	0,037
90							0,048	0,048
95							0,035	0,035
100							0,019	0,019

Table 3.4: Time of decolouration with thermo/UV/hydrogen peroxide process in time period of sampling from May to September 2005

Date	t [min]
11.05.05	75
16.05.05	75
23.05.05	85
30.05.05	45
13.06.05	70
20.06.05	80
27.06.05	100
average time	76
min time	45
max time	100

Table 3.5: Results of wastewater decolouration in thermo and UV part at wavelength 436 nm in time period from May to September 2005

Date	11.5.2005	16.5.2005	23.5.2005	30.5.2005	13.6.2005	20.6.2005	27.6.2005	average
Thermo part (%)	34,48	38,24	30,57	98,83	66,67	31,75	62,12	51,81
UV part (%)	56,90	57,64	66,31		24,30	59,26	32,68	49,52

Table 3.6: Results of wastewater decolouration in thermo and UV part at wavelength 525 nm in time period from May to September 2005

Date	11.5.2005	16.5.2005	23.5.2005	30.5.2005	13.6.2005	20.6.2005	27.6.2005	average
Thermo part (%)	56,00	47,37	40,26	100,00	77,85	37,17	64,54	60,46
UV part (%)	43,20	52,63	58,79		18,89	53,95	33,34	43,47

Table3.7: Results of wastewater decolouration in thermo and UV part at wavelength 436 nm in time period from May to September 2005

Date	11.5.2005	16.5.2005	23.5.2005	30.5.2005	13.6.2005	20.6.2005	27.6.2005	average
Thermo part (%)	54,55	50,00	42,52	100,00	56,59	32,34	64,91	57,27
UV part (%)	31,81	50,00	54,25		31,01	56,17	29,53	42,13

Table 3.8: Results of TOC values before and after decolouration with thermo and UV part in time period from May to September 2005

Date	TOC before decolouration	TOC after thermo part of decolouration	TOC after UV part of decolouration	% of TOC reduction
11.5.2005	119,8	131,9	54,77	54,3
16.5.2005	151	126,8	57,65	61,8
23.5.2005	148,5	141,4	50,1	66,3
30.5.2005	158,2	92,18	52,3	66,9
13.6.2005	130	119,6	59,33	54,4
20.6.2005	174,5	169,7	56,33	67,7
27.6.2005	190,9	171,1	64,4	66,3
average	153,3	136,1	56,4	62,5