Scientific paper

Multivariate Analysis and Chemometric Characterisation of Textile Wastewater Streams

Darja Kavšek,[1,*] Tina Jerič,[2] Alenka Majcen Le Marechal,[2] Simona Vajnhandl,[2] Adriána Bednárová[3] and Darinka Brodnjak Vončina[4]

[1] *Regional Technological Centre Zasavje, Chemical-Technological Laboratory, Nasipi 48, 1420 Trbovlje, Slovenia*

[2] *University of Maribor, Faculty of Mechanical Engineering, Smetanova 17, 2000 Maribor, Slovenia*

[3] *University of Ss. Cyril and Methodius in Trnava, Faculty of Natural Sciences, Nám. J. Herdu 2, SK-917 01, Trnava, Slovakia*

[4] *University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia*

** Corresponding author: E-mail: darjakavsek@gmail.com;*
Tel.: +386 2 2294 431; fax: +386 2 2527 774

Received: 15-02-2013

Abstract

The aim of this work was to design a quick and reliable method for the evaluation and classification of wastewater streams into treatable and non-treatable effluents for reuse/recycling. Different chemometric methods were used for this purpose handling the enormous amount of data, and additionally to find any hidden information, which would increase our knowledge and improve the classification. The data obtained from the processes description, together with the analytical results of measured parameters' characterising the wastewater of a particular process, enabled us to build a fast-decision model for separating different textile wastewater outlets.
Altogether 49 wastewater samples from the textile finishing company were analysed, and 19 different physical chemical measurements were performed for each of them. The resulting classification model was aimed at an automated decision about the choice of treatment technologies or a prediction about the reusability of wastewaters within any textile finishing or other company having similar characteristics of wastewater streams.

Keywords: Textile finishing wastewater, water-quality, chemometrics, multivariate data analysis, classification, wastewater treatment

1. Introduction

The textile industry is a very diverse sector in terms of raw materials, processes, products, and equipment.[1,2] Although there are a large variety of processes and technologies within the textile industry, this sector can be roughly categorized into dry and wet processing. Wet processing, also called textile finishing, is the most water, energy, and pollution-intensive, consuming up to 800 L of water per kg of fabric and a huge variety of chemicals (10% to over 100% of the cloths's weight).[2–4] The wastewater differs greatly in composition, due to the differences in processes (preparation, dyeing, finishing, sizing, and other operations), and the equipment.[5] In Europe, 108 million tons of wastewater is produced on a yearly basis and 36 million tons of chemicals and auxiliaries have to be removed from the textile wastewaters. These wastewaters are heavily charged with unconsumed dyes (up to 50%) and other chemicals (salts, acids, bases, surfactants, metals, organics, biocides, persistent organic pollutants, etc.). Metals like zinc, cobalt, chromium, mercury, copper and lead can also be found in textile wastewaters.

The textile finishing industry, in most cases, just neutralizes the wastewater and, without any other treatment on site, sends it to a municipal wastewater treatment plant.[6,7]

Therefore, the amount of water discharged and the chemical loads of the textile effluents are of major environmental concern throughout the textile finishing industry.[3,8] Besides, the recycling of wastewater is becoming a necessity, but it must be realised in a safe way, whilst maintaining product quality and process stability at the same time.[9] It is because of the diversities of processes and constant change (monthly, seasonally, yearly) in production that it is impossible to use only one treatment method or to find a treatment solution suitable for all finishing companies, as well as from financial point of view.

An individual approach is necessary and the characterisation of major waste effluents is important for finding the most appropriate wastewater treatment/or treatment train solutions. Chemometric methods were applied for the characterisation and discrimination of different wastewater samples.[10–18]

Textile waste-effluents were gathered from different textile processes, dyeing, bleaching, scouring, and washing. Firstly, dyes and different auxiliaries (organic acids, defoamers, diluents, oxidizing/reducing and fixing agents) are pollutants generated during the dyeing process. Bleaching is commonly used for removing the natural colouring of fibers. Auxiliary inorganic chemicals ($NaCl$, Na_2SO_4, Na_2SO_3, $NaClO$, $NaClO_2$, Na_2CO_3, Na_2SO_4, $Na_2S_2O_4$, $NaNO_2$, H_2SO_4, HCl, $NaOH$, $NaHSO_3$, H_2O_2, SO_2, trace metals) and surfactants are also used and released into the wastewater. Then, scouring is the process for removing different impurities from natural and synthetic materials. Scouring effluents contain oils, fats, waxes, minerals, detergents or soaps, and pesticides. Also de-sizing is the process of removing the size-chemicals from the textile. Wastewater from this process contains different additives, surfactants, enzymes, acids or alkalis, as well as the sizes themselves. And finally, washing is normally carried out in hot water in the presence of a wetting agent, and detergent. The detergent emulsifies the mineral oils and disperses the non-dissolved pigments.[6]

The intention of this work was to find correlation between different textile processes' outlets (Table 1) and the measured properties. In addition, a further task was to perform the classification of wastewaters into treatable and non-treatable wastewater streams for reuse/recycling purposes within any textile company, using different technologies including membrane and biological treatments, advanced oxidation processes (AOPs) or evapoconcentration.

2. Experimental

2. 1. Waste Water Samples

A standard method was used for sampling.[17] 49 textile wastewater samples were collected in 1000 mL polyethylene bottles at the outlets of each process machine described above and presented in Table 1, namely from dyeing, bleaching, scouring, de-sizing and washing. The number of samples is presented in the legend, below Table 1.

All glass and plastic wares used for sampling and analyses were rinsed with milli-Q water.

2. 2. Chemical Analyses

Standard analytical methods were used for the determinations of total nitrogen[20], chemical oxygen demand[21], turbidity[22], measurements of decolouration,[23] by measuring absorbance at three standard wavelengths according to environmental legislation: 436 nm, 525 nm, and 620 nm, and electrical conductivity.[24] The contents of Na and K were determined by atomic absorption spectrometry (AAS), using the PerkinElmer 1100 B atomic absorption spectrometer.[25,26] The determination of pH,[27] the metal contents[28], and the volatile and totally suspended solids[29] were also determined according to the standard ISO methods.

The absorbance was measured using an Agilent 8453 UV-Vis spectrophotometer (Agilent Technologies, US). The determinations of the Ba, Cu, Mn, Sr, Fe, Al, and Ca contents were carried out using inductively coupled plasma optical emission spectrometry (ICP-OES), Optima 5300 DV (PerkinElmer, US). The total nitrogen was determined using the Kjeldahl method and also with a TOC/TN analyser (multi N/C 2100/2100 S from Analytik Jena, Germany).

2. 3. Statistical Treatment of the Data

49 samples of textile wastewater from one Slovenian textile company were characterised in regard to 19 chemical and physicochemical properties (Table 2) . The enumerated variables were the vector representation of the components of each textile wastewater sample to be used for further chemometric analysis. Firstly, the exploratory analysis of available data was performed to identify outliers and to examine the normality of variables by using Kolmogorov-Smirnov test. The results from all measurements were explored by analysis of variance (ANOVA), non-parametric tests, correlation analysis, and multivariate data analysis methods.[30] The principal component analysis (PCA) and cluster analysis (CLU) were applied to examine the natural grouping of the textile wastewater samples as well as the relationships among the studied variables. The linear discriminant analysis (LDA) was used for the classification of textile waste waters into two categories according to their pollution and thus, the possibility of their treatment. All PCA and LDA calculations were accomplished with the IBM SPSS Statistics 21 and STATGRAPHICS Centurion statistical software; Microsoft Excel was used for the data preparation and results outputs.

3. Results and Discussion

3. 1. Exploratory Data Analysis

The available data of 49 textile effluent samples from 9 outlets (labelled as *OUT 1, OUT 2,…,OUT 9*) representing different processes and equipment (Table 1)

Table 1. Textile wastewater samples/outlets from different processes and machinery ($n = 49$).

Sample No.	Sample/discharge	Sample No.	Sample/discharge	Sample No.	Sample/discharge	Sample No.	Sample/discharge	Sample No.	Sample/discharge
1	DF/JET/BMB/OUT 1	11	DF/JET/REA/D/OUT 9	21	DF/SCH/REA/M/OUT 1	31	WF/JIG/OUT 4	41	DF/JET/REA/L/OUT 5
2	DF/JET/VAT/L/OUT 1	12	DY/SBD/OUT 1	22	DF/SCH/REA/M/OUT 3	32	WF/JIG/OUT 7	42	DF/JET/REA/L/OUT 6
3	DF/JET/VAT/L/OUT 4	13	DY/REA/D/OUT 1	23	DF/SCH/REA/M/OUT 5	33	BF/SCH/OUT 1	43	DF/JET/REA/L/OUT 7
4	DF/JET/VAT/L/OUT 8	14	DY/REA/D/OUT 6	24	DESF/JET/OUT 1	34	BF/SCH/OUT 4	44	DF/JET/REA/L/OUT 8
5	DF/JET/BBD/OUT 1	15	DY/REA/D/OUT 9	25	DESF/JET/OUT 2	35	BY/OUT 1	45	DF/JET/REA/L/OUT 9
6	DF/JET/VAT/M/OUT 1	16	DY/BBD/OUT 1	26	BF/JET/OUT 1	36	BY/OUT 5	46	WF/JET/OUT 1
7	DF/JET/VAT/M/OUT 4	17	DY/REA/L/OUT 1	27	BF/JET/OUT 4	37	DF/JET/REA/L/OUT 1	47	WF/JET/OUT 2
8	DF/JET/VAT/M/OUT 7	18	DY/REA/L/OUT 5	28	BF/JIG/OUT 1	38	DF/JET/REA/L/OUT 2	48	WF/JET/OUT 4
9	DF/JET/REA/D/OUT 1	19	DY/REA/L/OUT 9	29	BF/JIG/OUT 5	39	DF/JET/REA/L/OUT 3	49	WF/JET/OUT 5
10	DF/JET/REA/D/OUT 5	20	DF/SCH/BBD/OUT 1	30	WF/JIG/OUT 1	40	DF/JET/REA/L/OUT 4		

Legend:
DF dyeing fabric
JET jet (equipment/machine)
BMB black magic bleaching before dyeing
VAT vat dyestuffs
L light colour
BBD bleaching before dyeing
M medium colour
REA reactive dyestuffs
D dark colour
DY dyeing yarn
SBD scouring before dyeing
SCH schirm (equipment/machine)
DESF desizing fabric
BF bleaching fabric
JIG jigger (equipment/machine)
WF washing fabric
BY bleaching yarn
OUT 1 Outlet 1 (19 samples)
OUT 2 Outlet 2 (3 samples)
OUT 3 Outlet 3 (2 samples)
OUT 4 Outlet 4 (7 samples)
OUT 5 Outlet 5 (7 samples)
OUT 6 Outlet 6 (2 samples)
OUT 7 Outlet 7 (3 samples)
OUT 8 Outlet 8 (2 samples)
OUT 9 Outlet 9 (4 samples)

were analysed. Departures from normal distribution, identified by *Q-Q* plots and Kolmogorov-Smirnov test of normality ($p < 0.01$), were observed for all descriptors except for *pH*. In the case after examining the separated data of *OUT1* were examined, according to the Kolmogorov-Smirnov test, all the descriptors except *Fe*, *Turb*, and *COD*, were found to be abnormal ($p < 0.01$). Indeed, the large skewness and kurtosis were evident (Table 2); therefore also the non-parametric methods were applied for statistical examination of data.

3. 2. ANOVA and Non-parametric Tests

The effect of the target categorical variable (factor) *Outlet* upon the measured variables in the textile samples was investigated by ANOVA in order to discover statistically significant differences between the samples grouped into nine categories of *Outlet*. In addition, non-parametric tests of Kruskal-Wallis and Mann-Whitney (for pair wise comparisons) were carried out.[30]

In ANOVA, five descriptors were found significantly influenced by the *Outlet* factor (Table 3), namely *Sr*, *Fe*, *TN*, *pH* and *COD* ($p < 0.05$). Although, in case of the non-parametric Kruskal-Wallis test, the factor *Outlet* was found statistically significant ($p < 0.05$) in all variables except for *Mn, Al, A525* and *A620*. However, according to the Mann-Whitney test, the factor *Outlet* was significant in almost all variables except for *A620* when considering all pair-wise comparison of *Outlet* categories (Table 3). The first (*OUT 1*) and second category (*OUT 2*) could be considered as similar, because no statistically significant difference was proved. On the contrary, the first category (*OUT 1*) was markedly diverse from all other groups excepting *OUT 2*. Interestingly, *OUT 2* differed significantly only from *OUT 4* or *OUT 5* concerning few variables and similar situation was obvious when considering all other *Output* categories (Table 3).

3. 3. Correlation Analysis

Next step was to investigate the interrelations among all descriptors investigated by Spearman correlation analysis. Mutual correlation was sought for all the measured variables. The highest correlation coefficients (Table 4) for the data of 49 textile wastewater samples were found between the variables *A525* and *A436* ($r = 0.96$), between *Na* and *Cond* (0.88), between *TSS* and *VSS* (0.91), between *K* and *Ca* (0.82), and between *Sr* and *Ca* (0.95).

The content of sodium in effluent samples was very high, because during the processes such as dyeing with reactive or vat dyestuffs, different chemicals are added such as sodium chloride, sodium hydroxide, sodium carbonate and sodium sulphate. These chemicals were also responsible for high electrical conductivity due to the sodium, chloride, carbonate, hydroxide, and sulphite ions in the above mentioned samples.

Table 2. Basic statistical parameters for the distribution of measured chemical and physicochemical properties in textile effluent samples/outlets from one Slovenian textile company ($n = 49$).

Descriptor	Abbreviation	Units	Min	Max	Mean	Median	S.D.	Skewness	Kurtosis
Barium	*Ba*	mg L^{-1}	0	0.08	0.01	0.002	0.02	2.32	4.89
Copper	*Cu*	mg L^{-1}	0	0.30	0.03	0.002	0.06	2.69	7.79
Manganese	*Mn*	mg L^{-1}	0	0.23	0.03	0.007	0.06	2.24	4.08
Potassium	*K*	mg L^{-1}	0.12	620	70.73	3	161.52	2.65	5.85
Strontium	*Sr*	mg L^{-1}	0	0.29	0.04	0.013	0.06	2.58	7.47
Iron	*Fe*	mg L^{-1}	0	0.44	0.09	0.032	0.11	1.48	1.62
Aluminium	*Al*	mg L^{-1}	0	0.43	0.05	0	0.09	2.71	7.66
Sodium	*Na*	mg L^{-1}	80	17000	1544.96	300	3424.22	3.34	11.49
Calcium	*Ca*	mg L^{-1}	0	450.50	17.45	5.855	63.87	6.76	46.69
Total Nitrogen	*TN*	mg L^{-1}	1.03	297.12	38.11	4.360	70.67	2.36	5.16
pH	*pH*	–	2.1	12.60	8.09	8.200	2.81	–0.42	–0.78
Conductivity	*Cond*	μS cm^{-1}	105	83800	8004.84	1002	17254.77	3.15	10.35
Turbidity	*Turb*	NTU	1	168	25.22	8	38.51	2.23	4.56
Chemical oxygen demand	*COD*	mg L^{-1}	6	6700	1087.76	347	1511.62	1.88	3.34
Total suspended solids	*TSS*	mg L^{-1}	3	1183	99.98	28	215.43	3.87	16.00
Volatile suspended solids	*VSS*	mg L^{-1}	3	1042	81.08	22	197.90	3.93	15.77
Absorbance at 436 nm	*A436*	–	0	3.99	0.30	0.022	0.78	4.15	17.41
Absorbance at 525 nm	*A525*	–	0	4.14	0.28	0.290	0.83	4.24	17.93
Absorbance at 620 nm	*A620*	–	0	2.52	0.12	0.013	0.41	5.11	27.66

Table 3. Summary of investigated waste water samples with the mean values for each category of *Output*. The statistically significant results of Kruskal-Wallis test for variables are denoted bold ($p < 0.05$).

Descriptor*	**Outlet label/** category code								
	OUT 1/^{1}	**OUT 2/^{2}**	**OUT 3/^{3}**	**OUT 4/^{4}**	**OUT 5/^{5}**	**OUT 6/^{6}**	**OUT 7/^{7}**	**OUT 8/^{8}**	**OUT 9/^{9}**
Ba^{b}	0.02^{4,5,7,9}	0.03	0.00	0.01^{1}	0.00^{1}	0.00	0.00^{1}	0.00	0.00^{1}
Cu^{b}	0.06^{3,4,5,6,7,8,9}	0.01	0.00^{1}	0.03^{1}	0.02^{1}	0.00^{1}	0.00^{1}	0.00^{1}	0.00^{1}
Mn	0.06^{7}	0.06	0.00	0.01	0.01	0.00	0.00^{1}	0.00	0.00
K^{b}	168.64^{3,4,5,7,8,9}	53.67^{4,5}	1.23^{1}	1.44^{1,2}	4.96^{1,2}	21.64	0.41^{1}	1.11^{1}	1.63^{1}
Sr^{a,b}	0.08^{3,4,5,7,8,9}	0.05	0.01^{1}	0.01^{1}	0.01^{1}	0.02	0.00^{1}	0.0^{1}	0.01^{1}
Fe^{a,b}	0.17^{3,4,5,7,8,9}	0.11	0.01^{1}	0.05^{1}	0.05^{1}	0.08	0.02^{1}	0.00^{1}	0.00^{1}
Al	0.05	0.05	0.08	0.04	0.01^{6}	0.049^{5}	0.01	0.11	0.12
Na^{b}	3515.79^{4,5,7,8,9}	1133.33	310.0	238.57^{1}	231.86^{1}	300.00	96.67^{1}	95.00^{1}	127.50^{1}
Ca^{b}	38.70^{3,4,5,7,8,9}	15.68^{5}	2.67^{1}	2.63^{1}	3.39^{1,2,7}	6.45	0.29^{1,5}	1.13^{1}	2.26^{1}
TN^{a,b}	90.16^{3,4,5,6,7,8,9}	7.92	2.340^{1}	9.02^{1}	2.75^{1}	2.89^{1}	2.83^{1}	2.37^{1}	6.11^{1}
pH^{a,b}	9.83^{4,5,7,9}	7.63	9.40	7.50^{1}	6.93^{1}	7.65	60.30^{1}	6.20	5.10^{1}
Cond^{b}	18672.11^{4,5,6,7,8,9}	5950.67	1061.50	1218.14^{1}	484.86^{1}	511.50^{1}	427.0^{1}	435.0^{1}	599.25^{1}
Turb^{b}	47.21^{4,5,9}	50.33	3.0	10.29^{1}	7.86^{1}	4.50	8.67	2.50	3.75^{1}
COD^{a,b}	2289.32^{3,4,5}	628.67	57.50^{1}	326.14^{1}	242.57^{1}	247.00	337.33	308.0	424.75
TSS^{b}	217.47^{3,4,5,7,8,9}	110.33^{4,5}	5.0^{1}	20.43^{1,2}	14.43^{1,2}	41.50	13.33^{1}	7.00^{1}	11.25^{1}
VSS^{b}	175.26^{3,4,5,7,8,9}	68.0	8.0^{1}	17.00^{1}	13.57^{1}	58.0	13.33^{1}	4.00^{1}	11.25^{1}
A436^{b}	0.62^{4,7,8,9}	0.13^{4}	0.15	0.02^{1,2}	0.22	0.20	0.03^{1}	0.02^{1}	0.02^{1}
A525	0.55^{4,9}	0.07	0.09	0.01^{1}	0.22	0.43	0.02	0.02	0.02^{1}
A620	0.07	0.04	0.00	0.01	0.02	0.70	0.01	0.02	0.02

[*] Descriptors and their units are introduced in Table 2. [a] Statistically proved significant effect of *Outlet* on the descriptor (tested by ANOVA). [b] Statistically proved significant effect of *Outlet* on the descriptor (tested by Kruskal-Wallis test). [1,2,3,4,5,6,7,8,9] The median of the given category is significantly different from the median of the coded category (tested by Mann-Whitney test).

3. 4. Principal Component and Cluster Analysis

Principal component analysis (PCA) is an unsupervised method used for analysing the structure in multivariate data sets. It is a basic way used for characterising multidimensional data, providing a satisfactory representation of the studied objects by projecting the original data set from the high dimensional space onto the lower dimension space. Thus, PCA can transform data from multidimensional space into two dimensions without losing considerable amount of information. Moreover, in the PCA bi-plot, demonstrating simultaneously the objects

Table 4. Correlation coefficient matrix for selected descriptors in textile effluent samples. All statistically significant Spearman correlation coefficients ($p < 0.01$) are marked bold and the highly statistically significant Spearman correlation coefficients ($r \geq 0.70$) are subsequently marked with star (*).

	Ba	Cu	Mn	K	Sr	Fe	Al	Na	Ca	TN	pH	Cond	Turb	COD	TSS	VSS	A436	A525
Cu	**0.66**																	
Mn	**0.70***	**0.61**																
K	**0.43**	**0.47**	**0.43**															
Sr	**0.65**	**0.65**	**0.60**	**0.78***														
Fe	**0.62**	**0.59**	**0.74***	**0.55**	**0.67**													
Al	**0.53**	0.30	0.34	–0.02	–0.01	0.20												
Na	**0.37**	**0.41**	0.16	**0.61**	**0.64**	**0.41**	–0.04											
Ca	**0.66**	**0.60**	**0.66**	**0.82***	**0.95***	**0.72***	0.09	**0.62**										
TN	**0.58**	**0.61**	**0.52**	**0.61**	**0.71***	**0.67**	0.02	**0.66**	**0.68**									
pH	0.08	0.22	–0.07	**0.41**	0.19	0.29	0.12	**0.59**	0.22	**0.38**								
Cond	**0.48**	**0.53**	0.24	**0.66**	**0.72***	**0.51**	–0.03	**0.88***	**0.68**	**0.79***	**0.61**							
Turb	**0.65**	**0.54**	**0.63**	**0.43**	**0.52**	**0.73***	0.20	0.34	**0.56**	**0.66**	0.14	**0.40**						
COD	**0.45**	0.32	**0.37**	**0.45**	**0.66**	**0.53**	–0.22	**0.48**	**0.60**	**0.68**	0.09	**0.56**	**0.56**					
TSS	**0.64**	**0.57**	**0.49**	**0.59**	**0.70***	**0.60**	0.04	**0.56**	**0.71***	**0.67**	0.29	**0.67**	**0.62**	**0.63**				
VSS	**0.75***	**0.62**	**0.69**	**0.47**	**0.67**	**0.67**	0.22	**0.40**	**0.70***	**0.64**	0.10	**0.51**	**0.74***	**0.62**	**0.91***			
A436	0.24	0.24	0.10	**0.63**	**0.53**	0.35	–0.13	**0.66**	**0.53**	**0.53**	0.34	**0.61**	0.31	0.24	**0.40**	0.28		
A525	0.14	0.10	0.04	**0.58**	**0.44**	0.27	–0.22	**0.56**	**0.46**	**0.46**	0.25	**0.50**	0.26	0.23	0.34	0.22	**0.96***	
A620	0.16	0.23	0.17	**0.50**	**0.40**	0.30	–0.17	0.35	**0.40**	**0.48**	0.07	0.32	0.32	**0.39**	**0.41**	0.32	**0.66**	**0.74***

and the variables, it is possible to detect those variables, which are associated with the formed group of closely located objects (samples) and in this way the mutual relationships among the objects and variables can be discovered.[30,31]

The qualities of the textile wastewaters depended on the different textile processes and consequently, different wastewater outlets. According to the results of non-parametric tests, the first outlet (*OUT 1*) was always the most polluted one. All other outlets were less polluted as their composition was influenced by the rinsing processes. PCA was applied on a matrix composed of 49 × 19 elements, i.e. 49 rows represented the textile wastewater samples characterised by 19 variables. Column standardisation of the data was used, which meant that the mean values for each column were subtracted from the 49 individual elements and divided by the column standard deviation.

The PCA bi-plot of first two PC's accounting 60.0 % (PC1 36.6 % and PC2 23.4 %) of data variability is shown in Figure 1. The bi-plot displays the positions of the 49 wastewater samples, as well as 19 original variables. It can be seen that the first component PC1 was associated with a group of closely located, and hereby positively correlated, variables *COD*, *TSS*, *Sr*, *TN*, *Ca*, *Ba*, *Mn*, *Fe*, *VSS* and *K*. The second component PC2 mainly represented advanced descriptors *Cond*, *Na*, *A620*, *A525*, *A436* and *Ca* showing their positive correlation. The textile wastewater samples, separated from the main central cluster and distributed within the region of larger PC1, and also the PC2 values, were collected from the first wastewater outlet (labelled by number 1 in Figure 1). These textile wastewater samples were highly polluted since their *COD*, *TN*, and *VSS* were well-above the mean values.

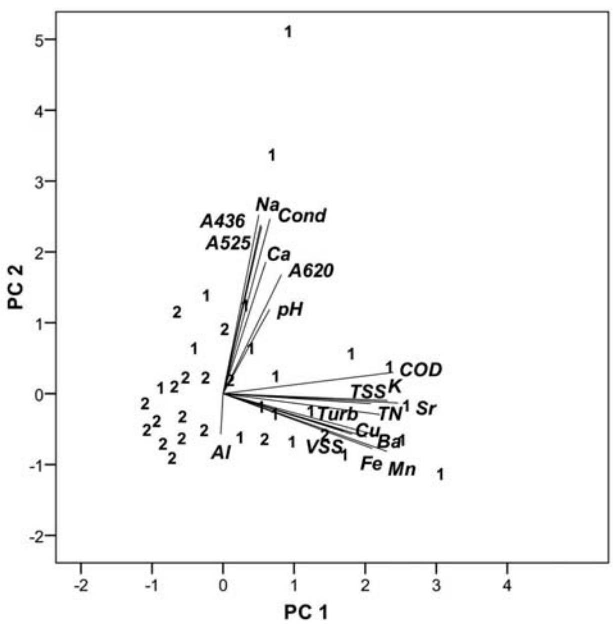

Figure 1. Bi-plot for the 49 textile wastewater samples from nine different textile effluent samples (outlets) (1 – first outlet *OUT 1*, 2 other outlets *OUT 2-OUT 9*). IBM SPSS Statistics 21.

Additionally, the results of PCA are in good agreement with the results of cluster analysis (CLU) when variable clustering was performed. Clustering techniques comprise unsupervised chemometric procedures that involve a measurement of the distances or the similarities between the objects to be clustered. The objects; but also the variables; are grouped in clusters in terms of their nearness or similarity.[32,33] The Ward's method, as the most effective agglomerative clustering algorithm, and the

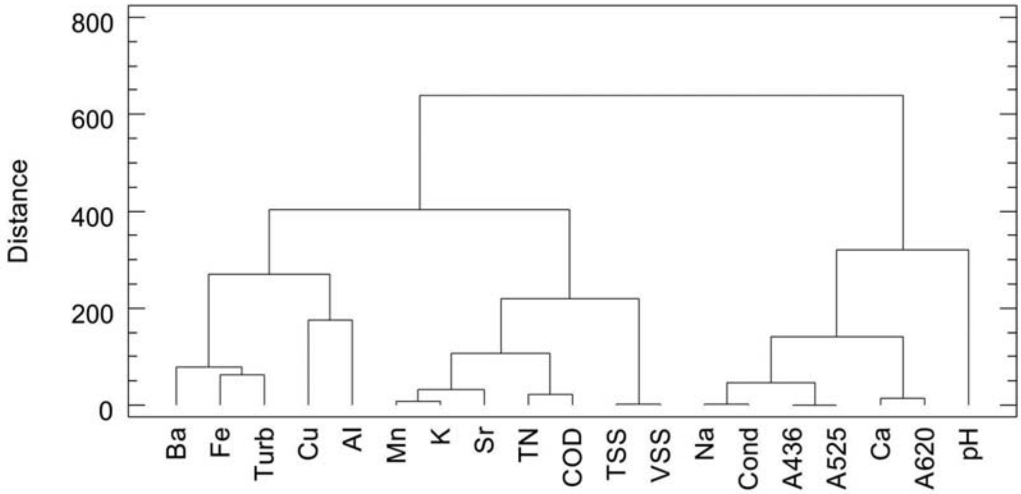

Figure 2. Dendrogram – the graphical output of the descriptors' clustering.

squared Euclidean distance (as the similarity measure) were applied (Figure 2).

In case when the clustering the textile effluent samples was made, a separate cluster of almost all samples originating from *OUT1* was recognizable in the grapfical output of CLU – dendrogram (the plot not shown). Thus, similarly to the PCA results, a natural grouping of the most polluted samples was found in the space of the analysed descriptors.

In addition, in case of clustering the descriptors, two separate clusters of the variables were observed, as in PCA. It is worth noting, however, that the role of PCA is not to separate the samples by categories, it should just display the natural proximities among the samples, among the descriptors, and also among the samples and the descriptors.

3. 5. Linear Discriminant Analysis

Linear discriminant analysis (LDA) is a frequently used supervised pattern recognition method in which a classification model is constructed using the data of the objects pre-categorized into known categories and the calculation algorithm is trained to discriminate the objects into the given categories (groups). It is based on the determination of linear discriminants, which maximize the ratio of between-class variance and minimize the ratio of within-class variance. LDA is to be considered as a dimension reduction method. For feature reduction, it is necessary to determine a smaller dimension hyper plane on which the points will be projected from the higher dimensional space. LDA selects directions, which achieves maximum separation among the given classes.[34]

According to chemometric analysis done all the results indicated that the more-polluted textile wastewater effluents came from the first outlets (*OUT 1*) after reactive dark, medium and light dyeing, vat medium dyeing, bleaching, scouring, desizing, and washing processes. All these effluents contained high- concentrations of inorganic salts (NaCl, Na_2CO_3, $Na_2S_2O_4$), dyestuffs (reactive, vat), alkalis (NaOH), stabilizers, auxiliaries, and different agents (dispersive, complex, reducing, oxidising). Textile outlet effluents from the above mentioned processes were highly concentrated and could be treated with proper technology, such as evapoconcentration. All other textile effluents (*OUT 2 - OUT 9*), less loaded with pollutants, especially inorganic salts, dyes, and alkalis, could be treated with advanced oxidation processes (AOPs) or membrane technologies, regarding to the maximum permitted value of certain parameters for selected technologies.

Processes using membranes provide very interesting possibilities for the separation of those hydrolysed dyestuffs and dyeing auxiliaries that simultaneously reduce the colouration and the ratio of biological to chemical oxygen demand of the wastewater; however, high concentrations of dyestuffs and salts in textile effluents have harmful effects on membranes.[35–38] The choice of the membrane process must be guided by the quality of the final product.[35] AOPs are used for the removal of COD, TOC, dyestuffs, phenol compounds, endocrine disrupting chemicals, and other recalcitrant organic chemicals from industrial and municipal wastewaters.[39] As known, AOPs are ineffective for treating highly-concentrated effluents, containing organic compounds with basic pH.[40]

For the purpose of classification of wastewater samples according to the possibilities of their treatment, altogether 49 textile samples were divided into two categories (Figure 3): (1) non-treatable wastewaters for recycling – more polluted textile wastewater effluents (originated from the first outlet (*OUT 1*) and (2) treatable wastewaters – less-loaded with pollutants (textile effluent samples from others outlets *OUT 2- OUT 9*). The stepwise selection method was used for reducing and optimising the set of 19 descriptors and the validation of the LDA model was accomplished by the leave-one-out method.

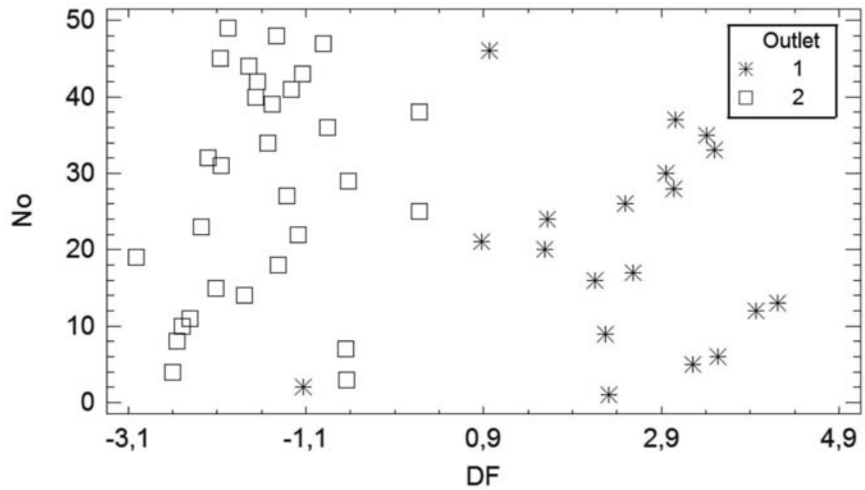

Figure 3. Graphical output of LDA for the 49 textile effluent samples which are well-separated in two clusters: (1) non-treatable and (2) treatable for recycling purposes.

The results of discrimination of waste water samples into two categories related to their treatment were satisfying using only eight variables as inputs: *TN*, *Fe*, *Sr*, *pH*, *Cond*, *Na*, *Mn* and *A525*. In total, the classification rate was 98.0 % (one sample was not correctly classified) by model building (training subset of data) and 95.9 % (two samples were not correctly classified) for leave-one-validation. Thus, the calculated discrimination function extracted the main information considering the textile wastewaters' pollution characterised in terms of numerous physicochemical properties analysed.

4. Conclusions

A quick and reliable method for the quality evaluation and classification of wastewater into treatable and non-treatable wastewater streams for reuse/recycling purposes, using foreseen technologies such as membrane processes, AOP, and evapoconcentration was presented. Several chemometric methods were applied in order to visualize multivariate data and to enable quick classifications of the textile wastewater samples, in regard to textile process wastewater outlets. This classification helped us to find the best treatment solution for the reuse of treated water in textile finishing processes (wastewater recycling). As expected, the most polluted textile wastewater effluents with high electrical conductivity derived from the first outlets after the dyeing process (reactive and vat dyes), then after bleaching, scouring, desizing and washing processes. These textile wastewater outlets could be treated with evapoconcentration, with regard to their complex compositions (high concentrations of inorganic salts, dyestuffs, alkalis, stabilizers, auxiliaries, and different agents). Other textile wastewater outlets were less loaded with pollutants, and could be efficiently treated with AOPs or membrane technologies.

5. Acknowledgements

The Operation part is financed by the European Union, European Social Fund. The operation is implemented in the framework of the Operational Programme for Human Resources Development for the Period 2007–2013, Priority axis 1: Promoting entrepreneurship and adaptability, Main type of activity 1.1.: Experts and researchers for competitive enterprises. We also acknowledge to the EU Commission, who enabled us to do this research within AquaFit4Use project, to the Ministry of Higher Education, Science and Technology of the Republic of Slovenia. We are grateful to Davide Mattioli and Selene Grilli, from Enea, for the measurements of some parameters.

The support of the Slovak grant agency VEGA 1/0233/12 is highly acknowledged.

6. References

1. I. I. Savin, R. Butnaru, *Environ. Eng. Manage. J.* **2008**, *7*, 859–864.
2. X. Ren, *J. Clean. Prod.* **2000**, *8*, 473–481.
3. E. Ozturk, U. Yetis, F. B. Dilek, G. N. Demirer, *J. Clean. Prod.* **2009**, *17*, 239–247.
4. M. M. Aslam, M. A. Baig, I. Hassan, I. A. Qazi, M. Malik, H. Saeed, *EJEAF Che.* **2004**, *3*, 804–811.
5. I. Bisschops, H. Spanjers, *Environ. Technol.* **2003**, *24*, 1399–1411.
6. J. Volmajer Valh, A. Majcen Le Marechal, S. Vajnhandl, T. Jerič, E. Šimon, in: P. Wilderer (Ed.): Water in the Textile Industry, Treatise on Water Science, Academic Press, Oxford, **2011**, pp. 685–706.
7. Newsletter, AquaFit4News, Issue 11, **2011**.
8. A. M. Kocabas, H. Yukseler, F. B. Dilek, U. Yetis, *J. Environ. Manage.* **2009**, *91*, 102–113.
9. M. Marcucci, G. Ciardelli, A. Matteucci, L. Ranieri, M. Russo, *Desalination* **2002**, *149*, 137–143.

10. A. Astel, S. Tsakovski, P. Barbieri, V. Simeonov, *Water Res.* **2007**, *41*, 4566–4578.
11. A. Astel, S. Tsakovski, V. Simeonov, E. Reisenhofer, S. Piselli, P. Barbieri, *Anal. Bioanal. Chem.* **2008**, *390*, 1283–1292.
12. M. K. Jamali, T. G. Kazi, M. B. Arain, H. I. Afridi, N. Jalbani, R. A. Sarfraz, J. A. Baig, *J. Hazard. Mater.* **2008**, *158*, 644–651.
13. R. R. Velinova, B. K. Koumanova, *Water Res.* **1995**, *29*, 2541–2547.
14. E. Tønning, S. Sapelnikova, J. Christensen, C. Carlsson, M. Winther-Nielsen, E. Dock, R. Solna, P. Skladel, L. Nørgaard, T. Ruzgas, J. Emnéus, *Biosens. Bioelectron.* **2005**, *21*, 608–617.
15. S. Carrer, R. Leardi, *Sci. Total Environ.* **2006**, *370*, 99–116.
16. T. Kowalkowski, R. Zbytniewski, J. Szpejna, B. Buszewski, *Water Res.* **2006**, *40*, 744–752.
17. Water quality-Sampling- Part 10: Guidance on sampling of waste water ISO 5667–01:**1996** (E).
18. V. M. Correira, T. Stephenson, S. J. Judd, *Environ. Technol.* **1994**, *15*, 917–929.
19. I. A. Oke, C. A. Okuofu, J. A. Otun, *J. Appl. Sci. Res.* **2006**, *2 (4)*, 209–216.
20. Water quality – Determination of Kjeldahl nitrogen – Method after mineralization with selenium, ISO 5663:**1984**.
21. Water quality – Determination of chemical oxygen demand, ISO 6060:**1996** (E).
22. Water quality – Determination of turbidity, ISO 7027:**1999**.
23. Water quality – Examination and determination of colour, ISO 7887:**1994** (E).
24. Water quality – Determination of electrical conductivity, ISO 7888:**1985**.
25. Water quality – Determination of sodium and potassium – Part 1: Determination of sodium by atomic absorption spectrometry, ISO 9964-1:**1993**.
26. Water quality – Determination of sodium and potassium – Part 2: Determination of potassium by atomic absorption spectrometry, ISO 9964-2:**1993**.
27. Water quality – Determination of pH, ISO 10523:**1996** (E).
28. Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES), ISO 11885:**2007**.
29. Water quality – Determination of suspended solids by filtration through glass-fibre filters, ISO 11923:**1998** (E).
30. D. L. Massart, B. G. M. Vandeginste, L. M. C. Buydens, S. De Jong, P. J. Lewi, J. S. Verbeke: Handbook of Chemometrics and Qualimetrics: Part A, Elsevier, Amsterdam, **1997**.
31. S. Sinha, A. Basant, A. Malik, K. P. Singh, *Ecotoxicol. Environ. Saf.* **2009**, *72*, 585–595.
32. K. Varmuza, P. Filzmoser: Introduction to Multivariate Statistical Analysis in Chemometrics, Boca Raton, CRC Press, **2008**.
33. R. G. Brereton: Chemometrics, Data Analysis for the Laboratory and Chemical Plant, John Wiley. & Sons, Ltd, Chichester, **2003**.
34. S. Rezzi, D. E. Axelson, K. Héberger, F. Reniero, C. Mariani, C. Guillon, *Anal. Chim. Acta* **2005**, *552*, 13–24.
35. B. Rameshu Babu, A. K. Parande, S. Raghu, T. Prem Kumar, *J. Cotton Sci.* **2007**, *11*, 141–153.
36. B. Zhang, S. Ma, *Mod. Appl. Sci.* **2009**, *3*, 52–58.
37. I. Koyuncu, *Desalination* **2002**, *143*, 243–253.
38. C. Tang, V. Chen, *Desalination* **2002**, *143*, 11–20.
39. A. S. Stasinakis, *Global NEST J.* **2008**, *10*, 376–385.
40. R. Munter, *Proc. Estonian Acad. Sci. Chem.* **2001**, *50*, 59–80.

Povzetek

Namen dela je postaviti hitro in zanesljivo metodo za ovrednotenje in klasifikacijo odpadnih vod v takšne, ki jih lahko obdelamo in ponovno uporabimo in takšne, ki jih ne moremo obdelati.
Za obdelavo velike količine podatkov smo uporabili različne kemometrijske metode, s katerimi smo poiskali skrite informacije, ki pripomorejo k povečanju znanja in izboljšanju klasifikacije. Podatki o procesih skupaj z analitskimi rezultati merjenih parametrov, ki opisujejo odpadno vodo iz posameznega procesa, omogočajo zgraditi model hitre odločitve za ločevanje različnih iztokov tekstilnih odpadnih vod.
V 49 vzorcih odpadnih vod tekstilne tovarne smo analizirali 19 različnih fizikalno kemijskih parametrov. Klasifikacijski model daje možnost avtomatskega odločanja o izbiri tehnologije čiščenja ali o napovedi ponovne uporabe odpadnih vod v kateri koli tekstilni ali drugi tovarni, kjer imajo odpadne vode podobne karakteristike.