# Quality Parameters of Offset Printing Wastewater

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***Abstract*—**Samples of tap and wastewater were collected in three offset printing facilities in Novi Sad, Serbia. Ten physicochemical parameters were analyzed within all collected samples: pH, conductivity, m - alkalinity, p - alkalinity, acidity, carbonate concentration, hydrogen carbonate concentration, active oxygen content, chloride concentration and total alkali content. All measurements were conducted using the standard analytical and instrumental methods. Comparing the obtained results for tap water and wastewater, a clear quality difference was noticeable, since all physicochemical parameters were significantly higher within wastewater samples. The study also involves the application of simple linear regression analysis on the obtained dataset. By using software package ORIGIN 5 the pH value was mutually correlated with other physicochemical parameters. Based on the obtained values of Pearson coefficient of determination a strong positive correlation between chloride concentration and pH ($r$ = -0.943), as well as between acidity and pH ($r$ = -0.855) was determined. In addition, statistically significant difference was obtained only between acidity and chloride concentration with pH values, since the values of parameter $F$ (247.634 and 182.536) were higher than $F_{critical}$ (5.59). In this way, results of statistical analysis highlighted the most influential parameter of water contamination in offset printing, in the form of acidity and chloride concentration. The results showed that variable dependence could be represented by the general regression model: $y = a_0 + a_1x + k$, which further resulted with matching graphic regressions.

***Keywords*—**Pollution, printing industry, simple linear regression analysis, wastewater.

## I. Introduction

A significant increase of scientific and technological development has led to a conspicuous pollution degree of basic natural resources. The importance of environmental protection and its improvement is a crucial issue which modern society needs to deal with. A great contribution to the victory in the battle of man against himself is to raise environmental awareness, thus creating a solid foundation for a new generation to become environmentally responsible and healthy people [1]. Changes in the environment caused by the strong development of economic activities and urban growth are distinguished as one of the major impacts of accelerated degradation of water resources. Contamination of aquatic ecosystems with discharge of treated or untreated wastewater threatens the environment and increases the risk of harmful substances for wildlife and humans [2], [3].

Water scarcity and pollution present a serious problem primarily because of increased human production activities. Industry is the largest polluter of water resources. After use, industrial facilities discharged water, which is often aggressive, loaded with silt and toxic substances [4], [5].

During the printing process water is used in all phases - as a fountain solution, cooling solution, washing solvents, as well as in the development process of the printing forms. As a result of these processes a large amount of wastewater is produced, which must be managed adequately in order not to endanger the environment. Monitoring, control and measurement of wastewater pollution in printing industry is of great importance, in order to set standard limit values of pollutants. Also a certain rules and regulations, which are necessary, are not clearly defined for the printing industry, which actually present the biggest problem in Serbia faced by all participants (management, utility inspection, workers) in printing production [6].

The wastewater of printing industry is enriched with different types of hazardous and harmful substances. The type and concentration of hazardous and harmful substances depends on the primary and secondary materials used in the production process, chemical reactions, process parameters, apparatus, intermediates and final products [7]. Printing wastewater can be enriched with various organic and inorganic compounds: benzene, aniline, cyclic nitro compounds, alcohols, esters, salts of organic acids, sodium chloride, salts of sulfuric and nitric acid, as well as iron and aluminum compounds [8]. Most of the printing companies discharge their wastewaters into recipients, especially in canal water, without appropriate treatment, although the legislation strictly requires the opposite. The waste material of printing industry should be appropriately removed and disposed, and thus prevent the disturbance of the environment. Therefore, it is especially necessary to monitor wastewater quality as well as to create a model for determination of the source and intensity of pollution. The best way to prevent contamination is complete transition to digital prepress. However, the cost of complete digitalization is enormous and many printing facilities still rely on photographic processes or automatic film developers and plates, in order to obtain the final copies and printing forms. Because of that, production organizations are forced to take effective measures to save water and reduce discharged effluent. Water pollution and limited possibilities of natural resources in Serbia demand improvement of wastewater, especially in the field of printing wastewater [9].

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TABLE I
PRINTING MACHINES

| Printing facility | Printing machine |
|---|---|
| 1 | Heidelberg Speedmaster 102-5-P3, B1 format |
| 2 | KBA Rapida 75, B1 format |
| 7 | Heidelberg Speedmaster 102 VP, B1 format |

Since the offset printing is a mainly used printing technique that covers 85% of the printing technique in Serbia, the objective of this study was to investigate the contamination level of offset printing wastewater, obtained from three facilities in Novi Sad, Serbia, through monitoring of various physicochemical parameters. In addition, a linear regression analysis was applied in order to examine the existence of quantitative agreement between investigated physicochemical parameters, as well as to establish the strength of the agreement and the nature of the relationship between the observed phenomena, as well as to highlight the most influential parameter of water contamination in offset printing.

## II. Materials and Methods

### A. Study Area

Three offset printing facilities from the territory of Novi Sad, Serbia, were selected for evaluation of wastewater quality. All printing facilities use a commercial offset printing process with outdated technology. Investigated printing facilities do not dispose their by-products according to regulations, and therefore they pollute the working and living environment in a smaller scale. Also, all printing facilities discharge wastewater into the recipient without treatment, whereas solid waste are disposed in landfills.

Printing machines, as well as all used materials in each printing facility are present in Tables I and II.

TABLE II
MATERIALS USED DURING THE PRINTING PROCESS

| Printing facility | Printing materials |
|---|---|
| | **Printing ink** |
| 1 | I-NET XL, EPPLE Druckfarben, Germany |
| 2 | SunLit Intense, Sun Chemical, India |
| 3 | Sheed Fed Ink TO140312, Toyo Ink, Japan |
| | **Printing plate** |
| 1 | Conventional printing plate Ipagsa, China |
| 2 | Agfa termostar 970, Agfa Graphic, Italy |
| 3 | Agfa termostar 970, Agfa Graphic, Italy |
| | **Fontain solution** |
| 1 | Isopropyl alcohol BF 212, Brentagof, Germany – 11% |
| | Buffer DH 20 10, Fujifilm, Belgium – 2,5-3,5% |
| | Water |
| 2 | Isopropyl alcohol K 30 DS, Brenntag, Austria – 5-6% |
| | Buffer Plano DS 4112, Fujifilm, Belgium – 3-4% |
| | Water |
| 3 | Isopropyl alcohol K 30 L, Brenntag, Austria – 9-10% |
| | Buffer Plano DS 4112, Fujifilm, Belgium – 3,5% |
| | Water |
| | **Cleaning soluion for manual plate washing** |
| 1 | Ofsetin DS Rotowash 60-1010, Fujifilm, Belgium |
| | Water |
| 2 | PC Plate multicleaner MC-E, Fujifilm, Belgium |
| | Ofsetin DS Rotowash 60-1010, Fujifilm, Belgium |
| | Water |
| 3 | Ofsetin P21, Cinkarna Celje, Slovenia |
| | Rubber coating P12, Cinkarna Celje, Slovenia |
| | activator for plate washing P211, Cinkarna Celje, Slovenia |
| | Water |
| | **Paper** |
| 1 | Mat kunstdruck 135g, Creator, Spain |
| 2 | Gloss kunstdruck 200g, Fegrigoni, Italy |
| 3 | Bio gloss 115g, Papirnica Vevče, Slovenia |

### B. Monitoring of Wastewater Quality

To test the quality of wastewater, one sample from each of the three printing facilities in Novi Sad, Serbia was taken. Also, a sample of tap water, which served as a blank sample, was collected from each printing facility. Quality assessment included the analysis of ten physicochemical parameters by using standard instrumental and analytical methods for samples of tap water and wastewater. The following physicochemical parameters were monitored: pH, conductivity, m - alkalinity, p - alkalinity, acidity, carbonate concentration, hydrogen carbonate concentration, active oxygen content, chloride concentration and total alkali content.

Conductivity and pH of tap water and waste water were monitored *in situ* by Multi pH/Cond/Temp 340i. Alkalinity, acidity, carbonate concentration, hydrogen carbonate concentration, active oxygen content, chloride concentration and total alkali content were determined by standard volumetric methods.

### C. Simple Linear Regression Analysis

Regression analysis involves identifying the relationship between a dependent variable and one or more independent variables. A model of the relationship is hypothesized, and estimates parameter values are used to develop an estimated regression equation. Various tests are then used to determine if the model is satisfactory. If the model is deemed satisfactory, the estimated regression equation can be used to predict the value of the dependent variable for given values of the independent variables [10].

Simple linear correlation is a measure of the degree to which two variables vary together, or a measure of the intensity of the association between two variables. In simple linear regression, the model used to describe the relationship between a single dependent variable y and a single independent variable x can be described with (1) [11]:

$$y = a_0 + a_1 x + k \quad (1)$$

where a0 and a1 present the model parameters and k is a probabilistic error term that accounts for the variability in y that cannot be explained by the linear relationship with x.

If the error term were not present, the model would be deterministic. In that case, knowledge of the value of x would be sufficient to determine the value of y.

## III. Results And Discussion

### A. General Physicochemical Parameters

The average values of physicochemical parameters, as the indicators of wastewater quality from three offset printing facilities are presented in Table III. Tap water was used as a blank sample, in order to compare the obtained values for the investigate physicochemical parameters.

Results obtained by experimental investigation give a clear view of all the examined parameters and indicate that the characteristics of the wastewater after the printing process differ significantly from tap water in every printing facility individually.

Increase of pH value is evident due to the reduction of buffering capacity of the concentrate as one of the main components of fountain solution. This change is occurred due to the intensification of the printing process and interaction between fountain solution and the active components of the printing inks and paper. Besides that, increased electrical conductivity resulted from greater absorption of the active components used in printing inks (pigments, fillers, and siccative), paper and anti-offset powder. A significant increase of acidity was observed in all analyzed wastewater samples, as a result of the presence of hydrolyzed salt or mineral acids.

TABLE III
THE AVERAGE VALUES OF PHYSICOCHEMICAL PARAMETERS OF WASTEWATER AND TAP WATER IN THREE PRINTING FACILITIES

| Printing facility | Parameter | Wastewater | Tap water | MAC[a] |
|---|---|---|---|---|
| 1 | pH | 7,2 | 5,9 | 6,8-8,5 |
| | Conductivity (µs/cm) | 1519 | 667 | 1000 |
| | Acidity (mg $CaCO_3$/L) | 208 | 6 | 100 |
| | m - Alkalinity (mg $CaCO_3$/L) | 40 | 32 | 100 |
| | p - Alkalinity (mg $CaCO_3$/L) | 0 | 8 | 100 |
| | $CO_3^{2-}$ (mg/L) | 0 | 16 | 100 |
| | $HCO_3^-$ (mg/L) | 60 | 16 | 100 |
| | $Cl^-$ (mg/L) | 397,04 | 25,60 | 200 |
| | $O_2$ (mg/L) | 12,8 | 6,4 | 50 |
| | NaOH (mg/L) | 200 | 80 | 150 |
| 2 | pH | 7,4 | 6,3 | 6,8-8,5 |
| | Conductivity (µs/cm) | 1469 | 662 | 1000 |
| | Acidity (mg $CaCO_3$/L) | 132 | 9 | 100 |
| | m - Alkalinity (mg $CaCO_3$/L) | 40 | 14 | 100 |
| | p - Alkalinity (mg $CaCO_3$/L) | 0 | 6 | 100 |
| | $CO_3^{2-}$ (mg/L) | 0 | 12 | 100 |
| | $HCO_3^-$ (mg/L) | 40 | 2 | 100 |
| | $Cl^-$ (mg/L) | 279,41 | 23,88 | 200 |
| | $O_2$ (mg/L) | 25,6 | 6,4 | 50 |
| | NaOH (mg/L) | 216 | 144 | 150 |
| 3 | pH | 7,0 | 5,4 | 6,8-8,5 |
| | Conductivity (µs/cm) | 1917 | 641 | 1000 |
| | Acidity (mg $CaCO_3$/L) | 434 | 10 | 100 |
| | m - Alkalinity (mg $CaCO_3$/L) | 30 | 24 | 100 |
| | p - Alkalinity (mg $CaCO_3$/L) | 0 | 6 | 100 |
| | $CO_3^{2-}$ (mg/L) | 0 | 12 | 100 |
| | $HCO_3^-$ (mg/L) | 30 | 12 | 100 |
| | $Cl^-$ (mg/L) | 319,76 | 27,73 | 200 |
| | $O_2$ (mg/L) | 64 | 6,4 | 50 |
| | NaOH (mg/L) | 144 | 64 | 150 |

[a]Maximum allowed concentration according to the Water Law of the Republic of Serbia [12]

In all analyzed wastewater samples p - alkalinity was equal to zero, whereas m - alkalinity significantly increased, probably due to the increased concentration of bicarbonate. Also, it was observed a significant increase of chloride concentration, oxygen, and total alkali content in wastewater samples of all printing facilities. The chloride concentration significantly exceeds the maximum allowed concentration probably due to the elevated chlorination of tap water during the disinfection process. It was also established that the conductivity, acidity and total alkali content exceed the maximum allowed concentration prescribed by the Water Law of the Republic of Serbia (Table III) [12].

TABLE IV
THE RESULTS OF SIMPLE LINEAR REGRESSION ANALYSIS

| Mutual dependence | Pearson coefficient | SD[b] | F[c] | Regression model |
|---|---|---|---|---|
| Conductivity and pH | -0.622 | 182.536 | 4.427 | Y = 1847,3693-51,7254X |
| Acidity and pH | -0.855 | 93.583 | 18.956 | Y = 445,5370-54,8728X |
| m - alkalinity and pH | 0.358 | 5.811 | 0.998 | Y = 34,8124+0,7817X |
| $HCO_3^-$ and pH | -0.123 | 14.421 | 0.108 | Y = 47,0412-0,6368X |
| $Cl^-$ and pH | -0.943 | 31.761 | 56.6513 | Y = 423,4545-32,1943X |
| $O_2$ and pH | -0.304 | 23.821 | 0.713 | Y = 45,8940-2,7097X |
| NaOH and pH | -0.201 | 247.634 | 0.296 | Y = 370,5434-18,1442X |

[b]Standard error of regression; [c]Parameter obtained from F-statistic

*B. Correlation among Physicochemical Parameters*

A simple linear regression analysis was applied in order to determine whether between a variation of the observed phenomenon exists a quantitative agreement (correlation), as well as to determine the strength of the agreement. Regression analysis was used to established the nature of the relationship, as well as a form of dependence between the observed phenomenon. For this purpose, a regression model that best expresses the quantitative correlation between the explored phenomena was used. In this statistical model a correlation between pH of wastewater in three printing facilities (independent variables) and electrical conductivity, m - alkalinity, acidity, $HCO_3^-$, $Cl^-$, $O_2$, NaOH (dependent variables) was observed. All mathematical and statistical calculations were made using software package ORIGIN 5.

Given that the measured values of p - alkalinity and $CO_3^{2-}$ concentration were equal to zero, they were not included in the statistical data analysis. The results of simple linear regression analysis are presented in Table IV.

The values of Pearson's coefficients (*r*) of -0.943 and -0.855 indicate a very strong correlation between chloride concentration and acidity with pH, respectively. A moderate correlation was obtained in the case of electrical conductivity and pH ($r$ = 0.622), whereas a weak correlation was dominant in most cases, between m - alkalinity, $O_2$ concentration, NaOH concentration and $HCO_3^-$ concentration with pH.

Parameter $F$ is calculated for $n$-$k$-$1$ degrees of freedom, where $n$ represent a sample size and $k$ is the number of parameters. For our data, value of $F_{critical}$ is 5.59. The interdependence between variables was statistically significant only in the case of acidity and chloride concentration with pH ($F$ value is greater than $F_{critical}$). All other investigated dependences resulted with values of $F$ statistic less than its critical value, which leads to the conclusion that these factors were not statistically significant. Based on the obtained results of statistical analysis, it can be concluded that acidity and chloride concentration are the most influential parameter of water contamination.

Graphics regression, which correspond to the obtained regression models (Table IV), are shown in Figs. 1-7.

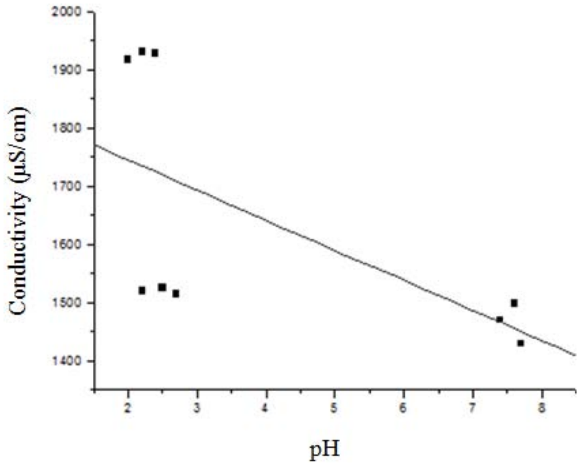


Fig. 1 Dependence of conductivity and pH

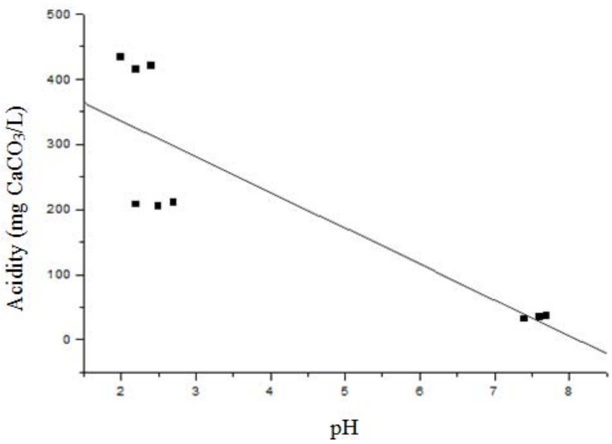


Fig. 2 Dependence of acidity and pH

In the two-dimensional graphs, the x-axis presents the pH value (independent variable), whereas y-axis presents the dependent variable. The resulting correlation shows an average stacking variation of investigated variables, presented by the general regression model: $y=a_0+a_1x+k$ (Table IV). In this way a quantitative agreement between the variations of variables is possible and thus a more accurate knowledge of their mutual relations is obtained.

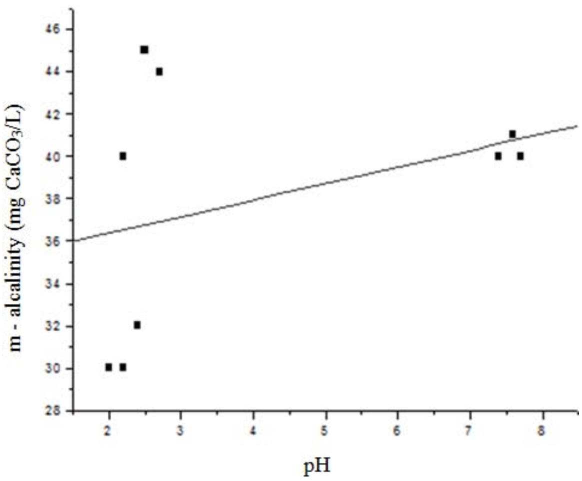


Fig. 3 Dependence of m - alkalinity and pH

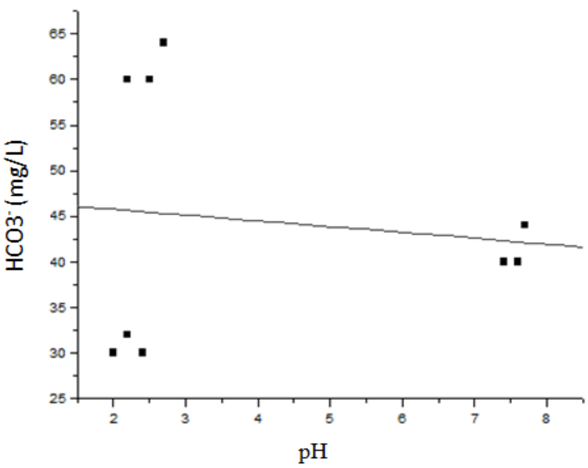


Fig. 4 Dependence of hydrogen carbonates concentration and pH

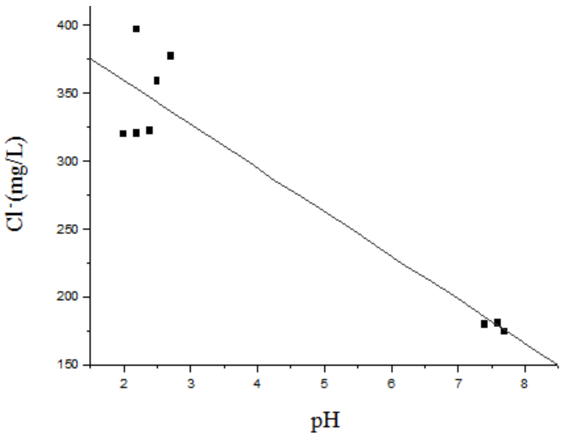


Fig. 5 Dependence of chloride concentration and pH

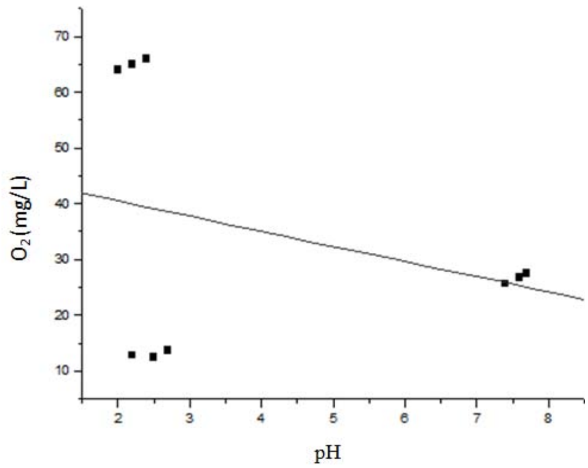


Fig. 6 Dependence of total oxygen concentration and pH

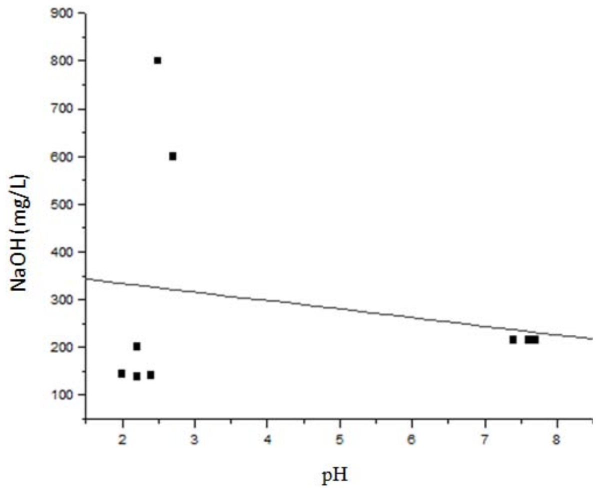


Fig. 7 Dependence of total alkali content and pH

## IV. Conclusions

The results of the quantitative identification of various physicochemical parameters confirmed expected contamination of wastewater samples, obtained after the offset printing process in three printing facilities from Novi Sad, Serbia. It has been determined that the conductivity, acidity, chloride concentration and total alkali content in the wastewater samples were higher than the maximum prescribed value by the Water Law of the Republic of Serbia.

Applied statistical analysis, simple linear regression, revealed a statistical significance only in a case of mutual interdependence between chloride concentration and pH, as well as between acidity and pH. For the same parameters the maximum value of Pearson's coefficients was obtained, indicating a strong positive correlation between them.

The obtained results and data classification, collected under real conditions, indicate the need for introduction of adequate eco-friendly replacements for certain toxic substances. In this manner, the physical and chemical characteristics of the materials can achieve a positive impact on the profitability and efficiency of technological processes, as well as on the quality of life and the working environment.

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