The determination of limit of tannery wastewater flowing to the wastewater treatment plant in Nowy Targ (Poland) in terms of the impact of chromium concentration on treated wastewater quality

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ABSTRACT

The aim of the study is to determine the maximum daily volume of tannery wastewater flowing into the wastewater treatment plant in Nowy Targ (Poland) in terms of the impact of chromium compounds on biological treatment processes. The analysis was based on the results of 81 samples of raw wastewater, after mechanical treatment and flowing into the receiver. The analysis covered the following indicators, that is, chromium (Cr), biochemical oxygen demand, chemical oxygen demand, total nitrogen and total phosphorus. The statistical analysis of the influence of chromium concentration on the values of individual indicators in treated wastewater was based on the Pearson linear correlation. Based on the analysis, it was found that the maximum concentration of chromium compounds flowing into the biological reactor should not exceed the value of 3.1 mg Cr/L. Moreover, as a result of the simulation, the maximum amount of incoming tannery wastewater (chrome wort) that can be discharged into the sewerage system was determined, on average daily 28.0 m³/d. As a practical guideline for the operator of the sewerage system in Nowy Targ (Poland), it is recommended to verify the issued water-legal permits for the discharge of tannery wastewater and, in the case of renewals, take into account the developed results.

Keywords: Tannery wastewater; Chromium; Organic and biogenic pollutants

1. Introduction

After the introduction of the guidelines contained in Directive 91/271/EEC of 21 May 1991 in Poland, activities aimed at ordering and improving the state of wastewater management were initiated. However, actions taken to protect the quality of surface waters and ground waters should not focus solely on the construction of new wastewater treatment plants and modernization of existing plants. An equally important issue is to maintain the adequate effectiveness and reliability of the functioning of the existing wastewater treatment plants, which are not (yet) economically qualified for modernization [1–4]. Many factors are affecting the instability of the elimination of pollutants in a wastewater treatment plant, which is not influenced by the plant’s operator or its influence is very limited [5–7]. Such factors include (mainly) a large unevenness of the wastewater inflow [8], low temperature of inflowing wastewater resulting from the discharge of meltwater (rainwater) into the sewerage system [9] or the introduction of industrial wastewater containing toxic elements to the sanitary sewerage network [10–13]. Toxic elements include, among others chromium ions, high concentration of which in the wastewater subjected to the treatment process, has a destructive effect on the metabolism of activated
sludge, which is the most common wastewater treatment technology in the world [24].

The elimination of limitation of this type of unfavorable factors must rely on the action called “fix the cause, not the effect” since the construction and exploitation of an installation for neutralizing industrial wastewater in the wastewater treatment plant is difficult and costly. It should also be emphasized that in such a situation, the increased costs of wastewater treatment are caused by all users (residents) of the sewerage system, which translates into social dissatisfaction. The construction of professional industrial wastewater pre-treatment systems located near industrial plants is connected with the fact that sewerage system receives wastewater with a lower concentration of pollutants, which is (largely) free of toxic substances [14–16]. In such a case, the amount of industrial (pre-treated) wastewater discharged into the sewerage system may be increased. The owner of the sewerage system should determine a total daily limit for the amount of industrial wastewater discharging to the sanitary sewerage system, which guarantees the maintenance of the full efficiency of the wastewater treatment processes in the wastewater treatment plant. This publication is a “voice in the discussion” on the issue of determining limits for the inflow of industrial wastewater to sanitary sewerage systems – on the example of the sewerage system in Nowy Targ (Poland), where there is a large problem with the disposal of industrial wastewater from furrier’s shops containing large amounts of chromium ions [17–19].

This study aims to determine the maximum daily volume of tanning wastewater flowing into the wastewater treatment plant in Nowy Targ in the aspect of the impact of chromium compounds on biological treatment processes. The detailed analysis covered the effect of the concentration of chromium ions in the mixture of domestic wastewater and tanning wastewater (flowing into the biological reactor) on the amount of organic and biogenic pollutants in treated wastewater in the aspect of indicating the maximum concentration of chromium ions, above which the concentration of these parameters in treated wastewater is higher than the permissible concentration. The analysis covered the concentration of chromium (Cr) ions in raw wastewater, in wastewater after mechanical treatment, and treated wastewater. In treated wastewater, the following compounds were analyzed: biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP).

The obtained results are a novelty in the science concerning the exploitation of wastewater treatment plants because they provide a tool, based on which the plant operator can determine the daily limit for industrial wastewater (containing above-standard amounts of chromium (Cr)) discharged into the sewerage system. The proposed methodology is universal and it can be adapted to any wastewater treatment plants system where there are problems with industrial wastewater. The analytical part of the study will verify the research hypothesis: there is a limited concentration of chromium ions in wastewater subjected to biological treatment processes with the use of the activated sludge method, as a result of which the permissible concentrations of pollutants in the wastewater flowing into the receiver are exceeded.

2. Materials and methods

2.1. Characteristics of the sewerage system and wastewater treatment plant

The sewage system in Nowy Targ has a length of 87.1 km. The sewerage network works in the gravitational system and only 1.7 km of the sewerage lines are in the pressure system. The sewerage network is made of PVC pipes and stoneware with DN diameters from 200 to 400 mm. The sewerage network is a sanitary network and it is intended to collect the domestic sewage. Currently, approximately 4,800 residential buildings, public buildings and service facilities are connected to the sewerage system. In addition, 60 legally operating furrier’s shops are connected to the sewerage system, from which industrial wastewater is discharged. In addition, wastewater from the tannery, which is difficult to estimate, is discharged into the sewerage network. Domestic sewage and wastewater flow into the collective mechanical-biological wastewater treatment plant with the designed capacity of 21,000 m³/d and assumed in the project PE = 116,000 inhabitants (Nowobilska-Majewska and Bugajski [13]).

The wastewater treatment plant in Nowy Targ was established in 1995 and is located at 49°29′N, 20°3′E (Fig. 1). The sewage from the municipal sewerage network is conveyed via a collector with a diameter DN = 1.2 m to a pumping station. The main pumping station operates two pumps with a capacity of 1,400 m³/h. The pumps lift wastewater to a height of 7.5 m for easy gravity flow through the entire process line. The wastewater flows from the pumping station to a screen room, where screenings are caught on two step-screens with a slot width of 3 mm and a rated power of 1.5 kW. Then, the wastewater flows into two sand traps, where mineral substances such as sand or gravel are sedimented. The sand separated by sedimentation is discharged into a sand scrubber separator, and after treatment and dewatering, is forced into a container. The wastewater leaving the sand traps is conveyed by an 800 mm DN pipeline to two basic settling tanks. The horizontal-flow settling tanks are 42.0 m long, 6.0 m wide and 3.6 m high. Basic sludge is collected in sludge hoppers and steadily removed to a gravity thickener. Biological treatment is performed using the sequencing batch reactor method. In the biological treatment section, three bioreactors are installed, which work in 8 h cycles. Each of them is 70 m long, 23 m wide and 4.5 m deep. Treated wastewater, after decanting, is discharged through a 1,000 mm DN collector pipe to the receiver, the Dunajec River. The scheme of the technological layout of the wastewater treatment plant is presented in Fig. 2.

2.2. Analytical and statistical methods

The research was carried out in a period of 24 months – from January 2017 to December 2018. During this period, 81 samples of raw wastewater, wastewater after mechanical treatment, and treated wastewater were analyzed. Places for the collection of wastewater samples (1, 2, and 3) are shown in the technological scheme of the wastewater treatment plant in Fig. 2. All wastewater samples were collected with the use of an automatic autosampler during the day – depending on the wastewater flow rate. The concentration
of chromium (Cr) ions was determined in raw (inflowing) wastewater and wastewater after mechanical treatment. On the other hand, in treated wastewater, the concentration of chromium ions, as well as BOD$_5$, COD, TN, and TP indicators, were determined.

Samples of wastewater were subjected to the physical-chemical analysis in accordance with reference methods set out in the applicable legal acts [20].

- chromium (Cr) – Hach DR 2800 spectrophotometer using LCK 313 cuvette tests;
- BOD$_5$ – oxygen measurement after 5 d incubation in temp. 20°C in OxiTop® 197 WTW;
- COD$_{Cr}$ – the dichromate test according to PN-ISO 6060:2006;
- TN – by PN-EN 25663:2001;
- TP – spectrophotometer Hach DR 2800 using cuvette tests LCK 349 and LCK 350.

In the most important part of the analytical study, the average concentration of chromium (W$_{Cr}$) in wastewater flowing to the biological reactor – depending on the amount
of municipal wastewater ($Q_1$) and tanning wastewater ($Q_2$), as well as depending on the concentration of chromium in municipal wastewater ($W_1$) and tanning wastewater ($W_2$) – was presented. The calculations took into account the $R$ factor, which determines the degree of chromium reduction at the stage of mechanical treatment. To calculate the concentration of chromium ions in the wastewater flowing to the biological reactor, Eq. (1) was prepared and used.

$$W_{Cr} = \frac{(W_Q Q_1 + W_Q Q_2)}{1 - R}$$

where $W_{Cr}$ – concentration of chromium in wastewater flowing to the biological reactor (mg Cr/L), $W_1$ – concentration of chromium in raw wastewater in the non-production period (mg Cr/L), $W_2$ – concentration of chromium in tanning wastewater (mg Cr/L), $Q_1$ – the average daily amount of wastewater in the non-production period ($m^3/d$), $Q_2$ – the average daily amount of tanning wastewater ($m^3/d$), $R$ – coefficient that determines the degree of chromium reduction at the stage of mechanical treatment.

In order to indicate the maximum concentration of chromium in the wastewater flowing into the biological reactor, which affects the above-normative values of the analyzed indicators in treated wastewater, the Pearson linear correlation analysis was used. In cases where the correlation turned out to be statistically significant at the level of $\alpha = 0.05$, diagrams of the dependence of the dependent variable (values of indicators in treated wastewater) on the independent variable (chromium concentration in wastewater flowing to the biological reactor) were developed and this dependence was described by the trend line equation. Then, the graphs show (horizontal line – green) the permissible value of a given indicator in treated wastewater. It was found that the maximum concentration of chromium in the incoming wastewater (vertical line – blue) is when the value of the indicator in treated wastewater is lower or equal to the permissible value.

Statistical analysis regarding Pearson’s linear correlation was performed using the “STATISTICA 8” (StatSoft, Inc., USA). The significance of the studied connection was checked with the student’s $t$-test at the significance level $\alpha = 0.05$.

3. Results and discussion

3.1. Concentration of chromium in raw wastewater after mechanical treatment and treated wastewater

In the analyzed period, in municipal wastewater flowing to the wastewater treatment plant, the median concentration of chromium was 7.23 mg/L (arithmetic mean: 7.17 mg/L). The range of chromium concentration of raw wastewater was from 0.69 to 20.90 mg/L. The concentrations of chromium at this level indicate that the inflowing wastewater has a significant share of wastewater from the tanning industry, because, in typical municipal wastewater, concentrations of chromium are at a much lower level or at the limit of quantification [21]. Furthermore, as indicated by the value of the coefficient of variation ($C_V = 47\%$), the concentration of chromium in raw wastewater was at the level of large differentiation according to the scale proposed by Wawrzynek [22]. The irregularity in the inflow of chromium compounds in raw wastewater is connected with the seasonality in the functioning of furrier’s shops plants, which discharge wastewater from (tanning) to the collective sewerage network system in Nowy Targ – this was characterized in the previous publications regarding the sewerage system in Nowy Targ [13,17,19]. For a detailed analysis concerning the concentration of chromium in raw wastewater, a histogram was prepared in Fig. 3. It presents the percentage frequency for the occurrence of chromium concentration in individual class ranges (5 classes), where the span of each range was determined at 2.5 mg/L. In the analyzed period, the concentration of chromium in inflowing wastewater most often ranged from 7.5 to 10.0 mg/L (33.3% of cases). In the range from 5.0 to 7.5 mg/L, 28.4% of cases were reported. Therefore, it can be said that the inflow of chromium compounds contained in the mixture of domestic and tanning wastewater to the plant in question is a problem because (as indicated in the literature) high concentrations of chromium in wastewater negatively affects for the wastewater treatment processes – as presented by Song et al. [23], Vaiopoulou and Gikas [24], Jyothi et al. [25] and Grace Pavithra et al. [26].

Raw wastewater, which is a mixture of domestic and tanning wastewater, is subjected to the mechanical wastewater treatment. As shown by the research results, the average degree of reduction (%) of chromium compounds after mechanical treatment is 39.3%, while the median is 42.1%. The characteristics regarding the concentration of chromium in wastewater after mechanical wastewater treatment are presented in Fig. 4. In this case, 4 class ranges (span: 2.5 mg/L) were developed. According to the diagram (Fig. 4), the concentration of chromium in wastewater after the mechanical wastewater treatment usually reaches the value from 2.5 to 5.0 mg/L, which constitutes 58% of cases. The concentration of chromium above the value of 5.0 mg/L was recorded in 27.2% of cases. Referring to the reports presented by Park et al. [27], which indicate that the concentration of chromium in wastewater above 2.0 mg/L negatively affects for wastewater treatment processes (with the use of the activated sludge method), in the analyzed case, it was stated that the concentration of chromium above 2.0 mg/L occurred in 72 out of 81 cases (89% of cases). Based on the coefficient of variation ($C_V = 43\%$), it can be concluded that the concentration of chromium in wastewater after mechanical wastewater treatment was significantly differentiated – according to the scale proposed by Wawrzynek [22].

In the treated wastewater, discharged to the Dunajec River, the concentration of chromium compounds in 35.8% of cases was higher than the permissible concentration, which is 0.50 mg/L (Fig. 5.). Taking into account the above information, it can be stated that in an annual period of time, in nearly 131 out of 365 d, the concentration of chromium in the wastewater discharged to the river was higher than the permissible concentration. Fig. 5 presents a histogram concerning the frequency of occurrence of chromium concentration in treated wastewater. The histogram covers 4 class ranges with a class span of 0.25 mg/L. As in the case of the concentration of chromium in raw and pre-treated wastewater, a large variation in the concentration of this
parameter was also found – \( C_v = 48\% \) [22]. It is important to emphasize that in effluents, the concentrations of chromium were recorded at the level of 1.0 mg/L (maximum value). This indicates that it is possible and advisable to take action, in the result of which concentrations of chromium compounds in the effluents will be below the acceptable limit.

3.2. Influence of chromium concentration on the concentration of pollutant indicators

By using the data on the concentration of chromium in wastewater flowing to the biological reactor and the concentration of chromium in wastewater discharged (treated wastewater) from the biological reactor, a statistical analysis of the Pearson's linear correlation was carried out. This analysis aimed to determine the strength of the relation between the two above-mentioned variables. It was stated that the correlation between the concentration of chromium in wastewater flowing to the biological reactor and the concentration of chromium in wastewater discharged from the biological reactor is \( r_{xy} = 0.70 \). In the scale proposed by Stanisz [28], it means a very high level of correlation. In the analyzed case, the correlation is statistically significant at the confidence level of \( \alpha = 0.05 \), and the test value was \( t = 8.688099 \). The equation describing the regression line (shown in Fig. 6) indicates that an increase in the concentration of chromium in wastewater flowing to the biological reactor by 1.0 mg/L causes an increase in the concentration of chromium in wastewater discharged from the reactor by 0.09 mg/L. Furthermore, as it results from the described dependence, in order to ensure that the concentration of chromium in wastewater discharged from the receiver is at the permissible level of 0.5 mg/L, the concentration of chromium in wastewater subjected to biological wastewater treatment processes should not exceed the value of 3.1 mg/L. In Fig. 6, the horizontal line (green) indicates the permissible concentration of chromium in treated wastewater, while the vertical line (blue) shows the concentration of chromium in wastewater flowing to the biological reactor, for which the concentration of this parameter in the treated wastewater will be at the maximum level of 0.5 mg/L.

In the next part of the study, the influence of chromium concentration in wastewater flowing to the biological reactor, that is, after the mechanical wastewater treatment, on the process of neutralizing organic and biogenic pollutants was analyzed. As it was shown in the previous work concerning the reliability of the functioning of the wastewater treatment plant in Nowy Targ, this facility is characterized by certain unreliability in the disposal of organic (BOD$_5$, COD) and biogenic (TN, TP) pollutants [29]. Therefore, there is a need to identify the reasons for the instability in the operation of the wastewater treatment plant in question in order to ensure that in the future the facility will be characterized by high reliability in terms of the disposal of pollutants. As reported by Campos et al. [30], Madoni et al. [31], and Mendrycka et al. [32], one of the main reasons for lowering the metabolism of activated sludge in the biological reactor is excessive amounts of chromium compounds in wastewater. In addition, the COD/BOD$_5$ dependence was “average” susceptible in 11.5%, while in 60% this susceptibility was on the average level, as described by Nowobilska-Majewska and Bugajski in the publication [33]. It should also be noted that the described dependence was not very diverse during the research period, which means that the production of
organic flowing into the biological reactor was at an even level. Therefore, an attempt was made to indicate the effect of chromium concentration in the wastewater flowing into the biological reactor on the values of organic and biogenic pollutants in the wastewater flowing out of the treatment plant.

In this case, the analysis covered the concentration of chromium (Cr) in the wastewater flowing to the biological reactor and values of organic (BOD$_5$, COD) and biogenic (TN, TP) indicators in the wastewater discharged from the biological reactor. Like in the case of the analysis of the correlation between the concentration of chromium compounds in wastewater flowing to the biological reactor and discharged from the reactor, the correlation coefficient was calculated for dependencies Cr$_{\text{inflow}}$/BOD$_5$$_{\text{outflow}}$($r_{xy} = 0.60$), Cr$_{\text{inflow}}$/COD$_{\text{outflow}}$($r_{xy} = 0.63$), Cr$_{\text{inflow}}$/TN$_{\text{outflow}}$($r_{xy} = 0.34$), Cr$_{\text{inflow}}$/TP$_{\text{outflow}}$($r_{xy} = 0.62$). In three cases, that is, dependence of chromium (Cr) compounds in wastewater flowing to the biological reactor on BOD$_5$, COD, and TP, the correlation dependence was at the level of high correlation [28]. These dependence are statistically significant at the confidence level of $\alpha = 0.05$. In the case of the Cr$_{\text{inflow}}$/TN$_{\text{outflow}}$ dependence, the correlation was at the average level [28] and it turned out to be statistically insignificant. Therefore, in further analytical considerations, Cr$_{\text{inflow}}$/TN$_{\text{outflow}}$ dependence was neither developed nor discussed.

In the case of the BOD$_5$ value, as indicated by the equation of the regression line in Fig. 7, an increase in the concentration of chromium in wastewater flowing to the biological reactor by 1.0 mg/L causes an increase in the BOD$_5$ value in wastewater discharged from the reactor by 4.35 mg/L. Hence, in order to ensure that the value of BOD$_5$ in wastewater discharged to the receiver is below the permissible value of 15 mg/L, the concentration of chromium in wastewater subjected to biological wastewater treatment should not exceed the value of 3.1 mg/L. In Fig. 7, the horizontal line (green) indicates the permissible value of BOD$_5$ in treated wastewater, while the vertical line (blue) shows the concentration of chromium in wastewater flowing to the biological reactor, for which the value of BOD$_5$ in the treated wastewater will be at the maximum level of 15 mg/L.

In the case of the analysis concerning the value of COD, the regression line equation in Fig. 8 shows that an increase in the concentration of chromium in wastewater flowing to the biological reactor by 1.0 mg/L causes an increase in the value of COD in wastewater discharged from the reactor by 15.99 mg/L. In the case of this parameter, in order to ensure that the value of this parameter in wastewater discharged to the receiver is below the permissible value of 125 mg/L, the concentration of chromium in wastewater subjected to biological wastewater treatment should exceed the value of 3.8 mg/L. In Fig. 8, the horizontal line (green) indicates the permissible value of COD in treated wastewater, while the vertical line (blue) shows the concentration of chromium in wastewater flowing to the biological reactor, for which the value of COD in the treated wastewater will be at the maximum level of 125 mg/L.

Concerning the analysis of TP concentration based on the regression line equation presented in Fig. 9, it was stated that an increase in the concentration of chromium in wastewater flowing to the biological reactor by 1.0 mg/L will cause an increase in the concentration of TP in wastewater discharged from the reactor by 0.23 mg/L. As it results from the diagram presented in Fig. 9, in order to ensure that the concentration of TP in wastewater discharged to the receiver reaches (at most) the permissible concentration level of 2.0 mg/L, the concentration of chromium in wastewater subjected to biological wastewater treatment should not exceed the value of
5.1 mg/L. In Fig. 8, the horizontal line (green) indicates the permissible concentration of TP in treated wastewater, while the vertical line (blue) shows the concentration of chromium in wastewater flowing to the biological reactor, for which the concentration of TP in the treated wastewater will be at the maximum level of 2.0 mg/L.

3.3. Determination of the maximum inflow of tannery wastewater

In summary of this section of the analysis, it should be stated that in order to ensure that the concentration of organic and biogenic pollutants in the wastewater discharged to the receiver does not exceed the permissible
concentrations specified in the water license, the concentration of chromium (Cr) in wastewater subjected to biological wastewater treatment (after mechanical wastewater treatment) should be lower than or equal to 3.1 mg/L.

Eq. (1) was used to answer the fundamental question: how much tanning wastewater can be added (average daily) to domestic wastewater flowing via the sewerage network system to the wastewater treatment plant. Based on the previous research conducted by Nowobilska-Majewska and Bugajski [13] and Nowobilska-Majewska and Bugajski [29], the amount of \( Q_1 \) = 14382 m³/d was adopted as the average daily amount of wastewater flowing into the wastewater treatment plant. Based on the results of analysis of wastewater samples collected during the non-production period (e.g., public holidays, Christmas, holidays), the median for the concentration of chromium was determined at the level of \( W_{1} = 0.9 \) mg Cr/L. Samples of tanning wastewater (chrome wort) were also collected (10 times) for analysis. In these samples, the median for the concentration of chromium (Cr) was determined at the level of \( W_{2} = 2317.5 \) mg Cr/L. The R coefficient, as the median of the degree of chromium reduction in the mechanical part of the wastewater treatment plant, was adopted at the level of \( R = 42.1\% \). The amount of tanning wastewater (chrome wort) \( Q_{2} \) was simulated at the level from 5 to 70 m³/d, with an interval every 5 m³/d (horizontal axis in Fig. 10). The reliable value, that is, the maximum concentration of chromium in wastewater flowing to the biological reactor (after mechanical wastewater treatment) was adopted at the level of 3.1 mg Cr/L, because (as shown in the previous analysis) this is the limit concentration of chromium, which guarantees that the examined indicators (Cr, BOD₅, COD and TP) in treated wastewater will be at the level of permissible values. As shown in the diagram in Fig. 10, in order to ensure that the concentrations of the examined indicators do not exceed the permissible values, the amount of tanning wastewater (wort) flowing (daily average) to the sewerage system in Nowy Targ should not exceed the amount of \( Q_{2} = 28.0 \) m³/d.

4. Conclusions

As a result of the conducted analysis, it was stated that one of the factors determining changes in the concentration of Cr, BOD₅, COD and TP in wastewater discharged from the biological reactor to the receiver (i.e., the Dunajec River) is the concentration of chromium in wastewater after mechanical wastewater treatment. After the simulation, it was determined that the maximum amount of tanning wastewater (chrome wort) that may flow into the sewerage network system is (daily average) \( 28.0 \) m³/d. Larger amounts of tanning wastewater or its unevenness in the combined of wastewater will result in higher unreliability in the disposal of the above-mentioned pollutants in the currently used technological system of the wastewater treatment plant in Nowy Targ. Thus, the thesis was verified, that is, in the analyzed sewerage system, the permissible concentration of chromium ions in the wastewater flowing into the wastewater treatment plant in Nowy Targ should be 5.7 mg/L, and in the wastewater subjected to the treatment process, the concentration of chromium ions is 3.1 mg/L. Based on the above information operator of the sewerage network system in Nowy Targ should verify the water-legal permits issued for furrier’s shops for the discharge of tanning wastewater to the sewerage system and determine their total daily average amount at the level of 28.0 m³/d. Simultaneously, it is advisable to install tanning wastewater pre-treatment plants near furriers shops in order to reduce the concentration...
of chromium compounds. This will allow increasing the inflow of tanning wastewater to the sewerage system.

References


