The Chlorination Impact of Wastewater Treatment Plants in the Danube River

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An appropriate appraisal of the water quality parameters has an essential contribution in identification of main pollution factors in a certain region. In Romania, the lower course of Danube River Basin covers more than 1,075 kilometres and a significant percentage of the population lives in this area and depends on the Danube for potable water, industry, agriculture, and transport. The biodiversity, species and habitats, is markedly significant, taking in account that the Danube is the largest uninterrupted wetland area in the world and one of the last relatively undisturbed regions of Europe. The main focus of this article is to analyze the capability of chlorine removal in the municipal wastewater treatment plants in five counties of Romania, starting from 2013 to 2017. The five years average of influent fluctuates from 77.56 mg/dm^3 to 111.03 mg/dm^3 comparing with 82.94 mg/dm^3 and 116.29 mg/dm^3 the average of effluent. It should be specified that the limit imposed by the European legislation is 500 mg/dm^3. Even if the measured values are below a quarter of the imposed limit, chlorinated wastewaters can be poisonous and may have a harmful impact on aquatic flora and fauna that are exposed to them, and consequently, that chlorination dechlorination might not be appropriate treatment approach for the protection of receiving waters.

Keywords: wastewater treatment, biological chlorine removal, water pollution

Halogenated organic compounds contain fluorine, chlorine, bromine or iodine atoms; The nature of the halogen bond as well as the tip of the atom, significantly influences the purification technology. Particular attention is paid to certain problems due to the existence of toxicity (carcinogenicity), after which it can be reached with O_3 and, as the case may be contribution to the care or have the phenomenon of global warming by reducing the ozone layer [1].

Chlorine is considered a variable chemical widely used in water disinfection and wastewater treatment. Chlorine is an intensive oxidizing agent and is the commonly chemical utilized for the disinfection and adjustment of microorganisms in potable water. Chlorination is appreciated to be the most significant technique for preventing the diffusion of waterborne disease [2,3]. It was concluded that an aqueous chlorine solution is adequate in impede bacteria, viruses and protozoa infections [4,5]. Chlorine can neutralize most biological contaminants through different mechanisms among which the most important are: disrupting the cell wall, modifying the permeability of the cell (the capability to enter water in and out by the cell wall), changing the cell protoplasm, restricting the enzyme activity of the cell, limiting cell reproduction. Chlorine is added to extirpate the bacteria and viruses that were not eliminated through the filtration process. [6].

Most of the significant characteristic of wastewater result from the existence of weak acids and bases and their salts. The wastewater treatment operation is done by different unit processes [7,8]. It can be certainly settled that one of the most relevant unit techniques, on the whole wastewater treatment process, is disinfection [23]. pH has a major effect on disinfection. By increases in pH, the contact period necessary for disinfection using chlorine increases. Frequent sources of acidity consist of mine draining, runoff from mine tailings, and atmospheric sedimentation. As the Cl^- ion, chloride is a main inorganic component in water and wastewater. Sources of chlorides in natural waters consist of (1) draining of chloride from stones and soils; (2) saltwater penetration in coastal zones; (3) agricultural, industrial, domestic, and human wastewater; and (4) intrusion of groundwater into sewage system adjoining to saltwater. In wastewater, the chloride quantity is larger than in fresh water for the reason that sodium chloride is a frequent part of the alimentation and passes unaltered by the digestive system. Whereas ordinary technics of waste treatment do not eliminate chloride to any appreciable percent, higher than ordinary chloride concentrations can be used as an indication that the water is being used for waste discharge [9].

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Chloride is discharged into the ecosystems through various industrial branches, agriculture and different activities. Even though numerous countries have ratified strict effluent discharge values for chloride, considering the accelerating issues concerning the noxiously effects of chloride, pollution is even too significant [10,11].

The comprehensive accomplishment of the Urban Waste Water Treatment Directive 91/271/ EEC imply all European Member States to assume an adequate wastewater treatment technique in order to protect the nature and human health [12].

The EU conformity percentage on collection of waste waters is 94.7 % average, a high value. Nonetheless, it should be noted that 88.7 % of EU waste waters are properly purified by secondary treatment and more rigorous treatment is utilized to waste water discharged in areas around 76 % of EU territory. The Water Framework Directive 2000/60/EC 2000 focus on improving the aquatic ecosystems and demands to Member States to ensure that ordinary environmental quality requirements and discharge limit values for specific sets or types of pollutants should be established as minimum requirements in European legislation [13].

Nevertheless, agriculture is the main source of pollution on water bodies, and the spread chlorine contamination is a substantial risk to surface and groundwater quality. According to [14] agriculture is a significant pollution source for freshwater, estuarial and coastal waters along with domestic sewage, industrial waste water and rainwater run-off – collectively [15].

Wastewater treatment plants should keep a certain remnant in the wastewater to assure bacterial destruction rate in the course of chemical purification. Since disinfection is the final process in a wastewater treatment plants previously the discharge, the residual is evacuated together with the treated water. Sediments of the oxidizing disinfectants have been considered to have a harmful on aquatic systems and in particular in the receiving waterbody [16].

The Danube collects most of the rivers in Romania except for some in Dobrogea, transporting approximately 60 million tons of alluvium and 200 billion m^3 of water annually. It has a special importance for: navigation, hydropower, fish farming, being also an important source of water for agriculture, industry and population.

Experimental part

Chlorine, sodium and boron resulting from irrigation water, absorbed by the plants with the soil-water, progressively accumulate in the leaves. Assuming that the noxious ions garner excessive concentrations, they produce chlorosis, bronzing and bring significant changes to leaves, initially at the leaf top, then edges and, in some severe situations, symptoms may extend to the mid-leaf area.

The use of chlorine is an important step in waste water treatment and plants must be equipped with appropriate disinfection equipment, when water is discharged into the river basins. In this article were analyzed five years datasets collected from municipal wastewater treatment plant (WWTP), in the South and South -Est part of Romania, more precisely from Giurgiu, Calarasi, Braila, Galati and Tulcea.

The studied regions, is a preponderantly agricultural. The agricultural production is significant, accounting for 15.86% of the national production. Agriculture has an important economic region, 40.4% of the employed population in the region are employed in this sector. 65% of the total area of the region is agricultural land. Agricultural crops are a main feature of the region, the first being maize production, secondly wheat production, grain legumes, vegetables and thirdly sunflower production. Horticulture is well developed, and fishing and aquaculture, along with fish processing and trade in fish and fish products, are traditional activities in these areas.

An important concern is the risk the Urban Waste Water discharge upstream with potential to generate microbial pollution. In order to prevent this hazard should assure adequate treatment and strict disinfection system with suitable monitors and alarms.

In principle, the treatment plants operate in the same regime:

- a mechanical treatment stage that is designed to mechanically purify the waste water entering the station: grit chamber, rare and dense gratings, and storage tanks, grease, primary clarifiers.
- biological stage: aeration tanks, secondary decanters and the waste water sent to the emissary,
- the dehydrated sludge is sent to the ecological deposit, (fig. 1).

There is numerous analytical technique that can be used for the analyze of residual free chlorine and substances resulting after the chlorine procedure, namely absorption spectrophotometry, iodometry, and electrochemical techniques. The majority of the frequent analytical methods for chlorine in water are influenced by chemical oxidation-reduction reactions. It should be highlighted that every analytical technique for chlorine depends on the total oxidizing potential of the sample being tested and is immediately subject to interferences from different oxidizing factors. Notwithstanding numerous analytical procedures have previously been established, unfortunately, there is no “absolutely correct” procedure for chlorine analysis that is unambiguous and selective for the free chlorine and chloramine items.

Determination of chlorine and residual chlorine

The water samples were collected from the five sites situated in the Danube river basin and were examined by the laboratory’s urban wastewater treatment plants. European standard SR ISO 9297/2001 is used for determination of chloride content. [17, 18,19]. The chlorine dataset was measured from 2013 to 2017.

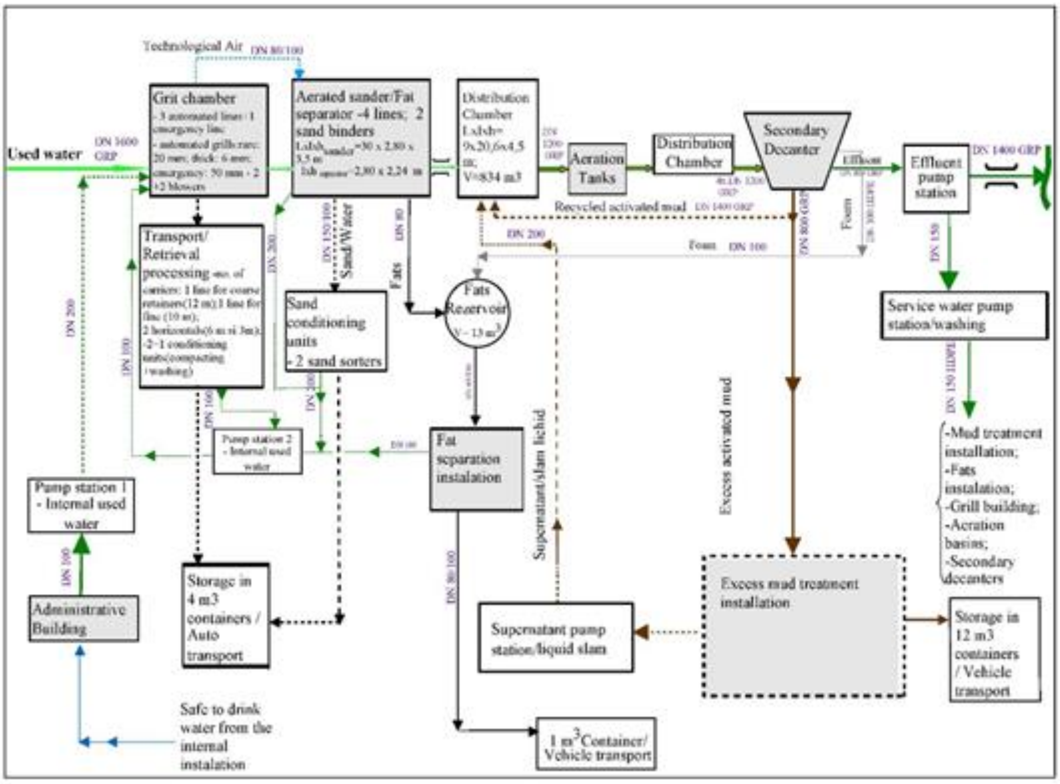

Fig. 1. General scheme for water course/line from a wastewater treatment plant

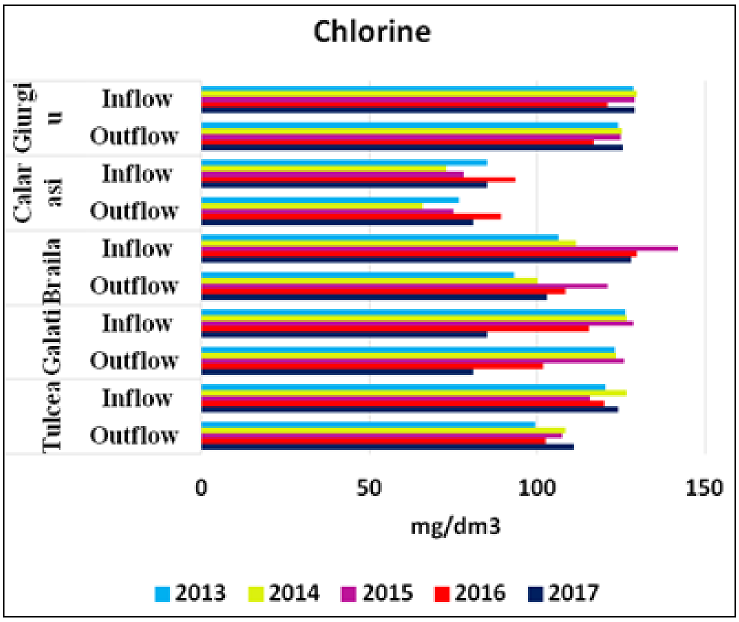

Fig. 2. The average values for 2013-2017 for chlorine, inflow and outflow

The presence of molecular chlorine in water is directly related to industry, and to the chlorine bound in soluble organic compounds, it is correlated, in most cases, with the pharmaceutical industries. If these forms of chlorine have a pollutant character and are monitored, the presence of chlorine is accepted at relatively high values and is a feature of the natural waters of the seas and oceans.

Residual chlorine is the excess chlorine that remains in the water after 30 minutes after contact with water.

The residual chlorine can be presented in two forms, namely:

- Free residual chlorine: elemental chlorine (Cl_2), hypochlorous acid (HOCl) or hypochlorite (ClO^-)
- Residual chlorine bound: chloramine (mono- and dichloramine)

These two forms of residual chlorine are important because their action and stability in water is different. The presence of residual chlorine in the water subjected to disinfection is of particular sanitary importance, indicating on the one hand that a sufficient quantity of chlorine has been introduced to ensure disinfection, and on the other that the integrity of the water distribution network is ensured. Free residual chlorine is a more valuable indicator than the bound one because it is much more sensitive.

Remarks

- the methods are used to determine the total residual chlorine (free chlorine + chlorine tied up);
- the method may be interfered with by other oxidizing substances which release iodine from potassium iodide;
- if the waters to be analyzed contain nitrates in large quantities or trivalent iron, instead of acetic acid the acetate buffer solution (6 mL acetate buffer for 100 mL of sample water);
- the method is used for high concentrations of residual chlorine (over 1 mg / dm^3).

Iodometric method

Principle of the method: Molecular chlorine releases iodine from potassium iodide in proportion to its concentration. The released iodine is titrated with a solution of sodium thiosulphate in the presence of starch as an indicator.

$$Cl_2 + 2KI \rightarrow I_2 + 2KCl \quad (1)$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI \quad (2)$$

Reagents

- potassium iodide, 10% freshly prepared solution;
- acetic acid solution 12%;
- 0.5% starch solution;
- 0.01 N sodium thiosulphate, which is prepared from 0.1% sodium thiosulphate solution

N by 10-fold dilution with boiled and cooled bidistilled water (the factor of sodium thiosulphate solution is determined against a solution of potassium dichromate with the same normality);

- acetate buffer solution: 102 mL normal acetic acid solution and 48 mL
- normal sodium nitrate solution is introduced into a 1000 ml graduated flask, filled to the mark with bidistilled water;
- Acetic acid normal solution is prepared from 57 mL glacial acetic acid and diluted to 1000 mL with bidistilled water;
- Sodium acetate normal solution is prepared from 136 g of sodium acetate, is introduced into a 1000 ml volumetric flask with a few mL of bidistilled water, then filled to the mark with bidistilled water.

Procedure

500 mL KI, 5 mL KI, 12.5 mL acetic acid and 5 mL starch solution are added to a porcelain capsule. Is mixed with a rod and titrated with sodium thiosulfate in a microburette until complete disappearance of the blue color.

Calculation principle:

$$mg\ Cl \frac{residual}{dm^3} = \frac{V_1 \cdot f \cdot 0.355 \cdot 100}{V} \quad (3)$$

where:

V_1 - mL 0.01 N sodium thiosulphate solution used for titration;
f - factor of 0.01 N sodium thiosulphate solution;
0.355 - the equivalent in mg of chlorine of one mL of 0.01 N sodium thiosulphate solution;
V - the amount of water to be analyzed, in mL.

Determination of residual chlorine with N, N-diethyl-p-phenylene diamine

Principle of the method: N, N-diethyl-p-phenylene diamine (known as DPD) reacts with chlorine or tri-iodide when intense red coloration results from the free radical formed; it is titrated (reverse titration) with the ferrous ion until the solution is discolored. DPD reacts rapidly with chlorine. The reaction with monochloramine is slow and concentration dependent and the presence of $HgCl_2$ apparently inhibits this reaction probably due to the formation of a non-reactive Hg (II) - monochloramine complex.

On addition of iodide reacts faster monochloramine forming the tri-iodide by reaction with DPD red color develops. The reaction with dichloramine is slow and requires large amounts of iodide.

The DPD solution is stored in acidic environment to avoid oxidation due to atmospheric oxygen, the reaction being catalyzed by the basic medium. It is recommended to periodically replace the solution (approximately one month). The neutral buffer solution for the reaction of chlorine or tri-iodide with DPD should be added at the time of analysis.

The presence of oxidants such as oxygenated water, manganese oxidizing species and persulphates strongly interferes with the oxidation of iodine.

For the reaction of chlorine or tri-iodide with DPD a neutral buffer will be added at the time of reaction. The limit of detection is 18 μg / L.

Reagents

- Phosphate buffer solution: dissolve 24 g of anhydrous Na_2HPO_4 and 46 g of anhydrous KH_2PO_4 in pure water. To this solution was added 100 mL of distilled water in which 800 mg of Na_2-EDTA was dissolved, then 20 mg of $HgCl_2$ was added to inhibit the development of microorganisms. Make up to 1 L with water;
- Dissolve 1 g of N, N-diethyl-p-phenylenediamine oxalate in aqueous solution containing 2 mL conc. H_2SO_4. and 200 mg Na2-EDTA dihydrate. Make up to 1 liter. The resulting solution is stored in well-closed brown glass;
- Iron and ammonium sulphate used as titrant: dissolve 1.106 g Fe $(NH_4)_2$ (SO_4)v · 6H2O in acidified water with 1/4 mL concentrated H_2SO_4 and make up to 4 liters;
- Solid potassium iodide.

Procedure

- 5 mL of buffer solution and DPD indicator solution was introduced into an Erlenmeyer flask and then 100 mL of the sample to be analyzed and stirred;
- For free residual chlorine: quickly titrate with ammonium sulphate and iron (II) until the red color disappears (volume A);
- For monochloramine: In the solution of point (a) add a small amount of potassium iodide and mix. Continue titration until the red color disappears again (volume B);
- Dichloramine: add approx. 1 g KI to the solution titrated in item (b) and mix.

After two minutes continue titration until the red color disappears (volume C).

At high concentrations of dichloramine, if there is color change after 2 minutes, the reaction is incomplete. Half the amount of potassium iodide may be used for low concentrations of dichloramine. For the purpose of representing graphically the yearly dispersion of chloride were used ArcGIS, a geo-statistical program, explicitly, the Spline interpolation module. ArcGIS may create optimal areas from sample data and estimate different types of predictions. Dataset of spatial coordinates can be disposed bi or three dimensional as random points, regular grid, or as centroids of polygons [20].

The Spline tool use an interpolation technique that define data implementing a mathematical algorithm that reduce the general surface curvature, subsequent in a plain surface that passes exactly among the input points. Selection of the convenient mechanism is determined by the modeling requires, information of about the mechanism operate, and the sample data collection. This method is a superior tool to generate various surfaces for example elevation, hazardous waste sites, polluted or degraded bodies of waters, Ocean Conditions / Temperature, air pollution levels, or pollution concentrations [21, 22].

The following formula, applied for the Spline tool, are used the surface interpolation:

$$S(x,y) = T(x,y) \sum_{j=0}^{n} \lambda_j R(⟦r)⟧_j \tag{4}$$

where:

j = 1, 2, ..., N.

N is the number of points.

λ_j are coefficients found by the solution of a system of linear equations.

r_j is the distance from the point (x,y) to the j^{th} point.

T(x,y) and R(r) are defined separately, depend on the selected alternative.

Results and discussions

For the purpose of analyses the chlorine diffusion in the medium and lower part of the Danube river basin, a five years data values measured from 2013 to 2017 was used. The yearly average was revealed in order to point out the efficiency of urban wastewater treatment plant, indicating the inflow and the outflow concentration of chloride.

Chemical treatment (chlorine) is one of the main adequate techniques for regulating biological growths, muck and bacterial development, although is expensive and necessitates a thorough management to utilize it cautiously. Chlorine destroys the organism, oxidizes the biotic matter and may necessitate filtering or flushing of the water line course to remove the organic constituents.

Evaluating the chloride concentration, it is obvious all values, in the entire area, do not exceed the limit, 500 mg/dm^3 established by the European legislation. Analyzing the outflow chloride, figure 2 point out a higher concentration, 125.75 mg/dm^3 in Galati in 2015, value comparable to 125.33 mg/dm^3 measured in Giurgiu in 2017.

120,97 mg/dm^3 is the highest outflow value measured in Braila in 2015, when 141,72 mg/dm^3 was the inflow chloride concentration.

For the purpose of getting a regional analysis for the entire period, the five years average was calculated. 114.31 mg/dm^3 is the inflow chloride concentration and 9.77 mg/dm^3 is the difference between inflow and outflow, indicating the importance of wastewater treatment before being discharged into the Danube basin.

Graphical analysis of pollutants or other substances and their dispersion in water plays a significant role, especially for decision makers. Annually maps were performed a spatial interpolation using ArcGIS software in order to obtain a visual image of chloride spreading. The geographical representation of chloride is important to achieve a general presentation of the entire zone and to precisely evaluate the impact of chloride on the Danube river basin.

Figure 3 is a visual observation that points out, for each urban area, higher values of chloride downstream the wastewater area. The largest concentration of inflow chloride is 127.42 mg/dm^3 the five average from Giurgiu, while 82.97 mg/dm^3 is the lowest inflow average from Calarasi. 2013 is the year when 3 of 5 urban wastewater plant had higher values, namely Giurgiu, Galati and Braila. The considered area in this article is an agricultural one and even if the chlorine concentration is well below the imposed limits, it is extremely important that the water entering the treatment plant be analyzed and treated.

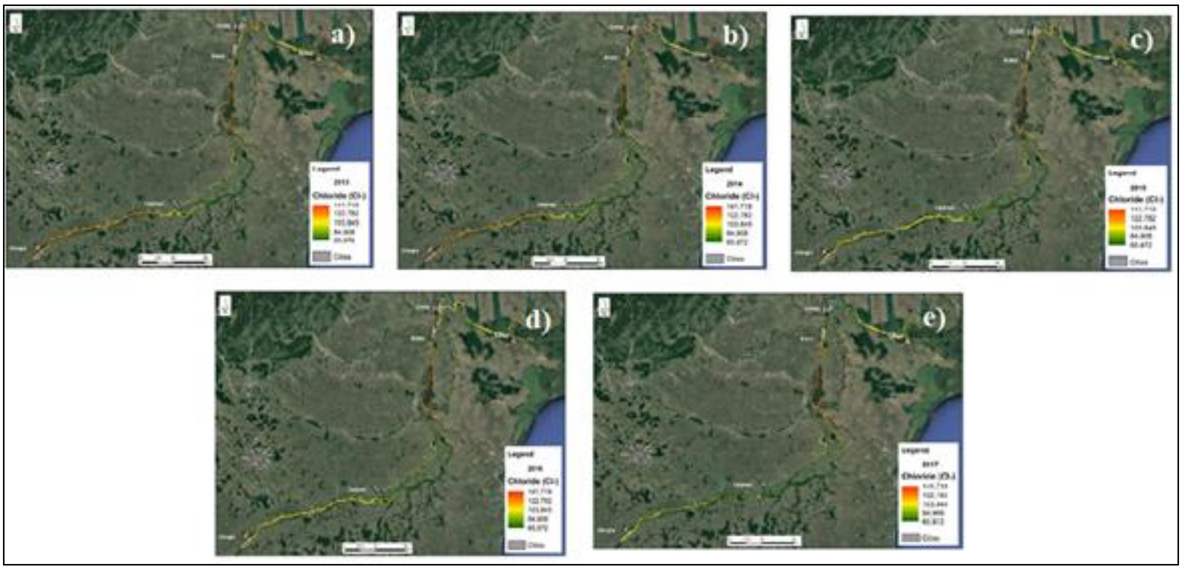

Fig. 3. Chlorine a) 2013; b) 2014; c) 2015; d) 2016 and e) 2017

Calarasi is the urban area with lowest chloride concentration, with average ranging from 65.97 mg/dm^3 in 2014 to 89.17 mg/dm^3 in 2016. An explanation may be related to number of inhabitants, Calarasi and Giurgiu are the smallest cities of the analyzed area.

Conclusions

The long-term chloride measurements indicate that the monitoring of chloride is essential even if, the difference between effluent and influent is not so significant. The five years average of south and south east regions for influent chloride is 114.31 mg/dm^3 comparing with 104.54 mg/dm^3 the average of effluent.

Advanced wastewater treatment consists is different techniques and operations that remove more pollutants (suspended and decomposed substances) from wastewater than are eliminated through standard biological treatment. In other terms, advanced wastewater treatment is the utilization a procedure or multiple operations that follows secondary treatment.

Furthermore, to fulfill the requirements of water quality standards, treatment equipments use advanced wastewater techniques for diverse reasons, more than that conventional secondary wastewater decontaminate is frequently not adequate to conserve the aquatic environment. Advanced wastewater treatment can eliminate more than 99% of the contaminants from untreated sewage and can generate an effluent approximately potable (drinking) water quality. Definitely, advanced treatment has a cost. The price of advanced treatment is very raised (frequently doubling the expense of secondary treatment). Advanced wastewater treatment is not unusual. These treatment procedures can be physical, chemical, or biological. The particular method used is determined by the scheme of the treatment and the quality of the effluent requested.

In Romania, insufficiently biological decontaminate of waste water has been considered as one of the essential pollution factors in the Danube and Black Sea area. Regarding the agricultural techniques, continuous chlorine inoculation is an excellent method, however may be high -priced for most general application. Its efficiency is related with the pH of the water, with more chlorine required at higher pH.

This article highlights an example of how geographic information system (GIS) software may be used to create a chlorine dispersion maps for regional ‐ scale.

References

1.ZAELKE. D., BORGFORD-PARNELL. N., Journal of Environmental Studies and Sciences, June 2015, Volume 5, Issue 2, p. 69–175.
2.KODERA. F., UMEDA. M.., YAMADA. A., Anal. Chim. Acta 2005, 537, 293-298.
3.ENE, M.D., JIPA, I., MARIA, G., STOICA-GUZUN, A., STROESCU, M., Rev. Chim. (Bucharest), **62**, no.2, 2011, p. 227.
4.OOMORI, T.; OKA, T., INUTA, T., ARATA, Y., Anal. Sci. 2000, 16, p.365-369.
5.***Centre for Affordable Water and Sanitation Technology, 2009, Household Water Treatment and Safe Storage Fact Sheet 4.2 Chlorine (Sodium Hypochlorite), Calgary, Canada.
6.SPELLMAN. F. R., Handbook of Water and Wastewater Treatment Plant Operations, Third Edition CRC Press Taylor & Francis Group, 2014
7.DEGREMONT, Water Treatment Handbook, 5th edition, 1, Lavoisier, Paris, 2007
8.BĂLĂNICĂ. DRAGOMIR. M. C., SIMIONESCU A. G., POPA C. L., BICHESCU C. I., MUNTENITA C., A Medium-term Analysis of Wastewater from an Agricultural Area Rev. Chim. (Bucharest),**70**, no. 4, 2019, p.1664-1666.
9.MARIA, C., TOCIU, C., MARIA, G., Chemical Papers, 67, no.2, 2013, p.173.
10.ASANO. T., BURTON. F. L., LEVERENZ. H. L., TSUCHIHASHI. R., TCHOBANOGLOUS. G., Water reuse: issues, technologies, and applications, Metcalf & Eddy, ISBN-13: 978-0-07-145927-3, 2007
11.***Water Environment Federation. Design of Municipal Wastewater Treatment Plants. Liquid processes, 4th ed.; WEF Manual of Practice No. 8; American Society of Civil Engineers & WEF: Reston, VA, USA, 1998; Volume 2, ISBN 0-7844-0342-2
12.***EC Directive. (1991), Directive concerning urban waste water treatment. Directive 91/271/CEC
13.9th implementation report (2017) https://ec.europa.eu/environment/water/water-urbanwaste/implementation/implementationreports_en.htm
14.MUNTENITA. C., BĂLĂNICĂ. DRAGOMIR. M. C., SIMIONESCU. A. G., STANCIU. S., POPA. C. L., The Efficiency of Biological Total Phosphorus Removal Process Rev. Chim. (Bucharest), **70**, no.6, 2019, p.1920-1923
15.SORLINI. S., BIASIBETTI. M., GIALDINI. F., COLLIVIGNARELLI. M.C., How can drinking water treatments influence chlorine dioxide consumption and by-product formation in final disinfection? Water Sci. Technol. Water Supply 2016, 16.
16.PAPA. M., BERTANZA. G., ABBÀ. A., Reuse of wastewater: A feasible option, or not? A decision support system can solve the doubt. Desalination Water Treat. 2015.
17.***SR EN ISO 7393- 1:2002; Water quality. Determination of free chlorine and total chlorine. Part 1: N, N-diethylphenylene-1,4-diamine titrimetric method
18.***SR EN ISO 7393- 2:2002; Water quality. Determination of free chlorine and total chlorine. Part 2: N, N-diethylphenylene-1,4-diamine colorimetric method for routine control
19.***SR EN ISO 7393- 13:2002 Water quality. Determination of free chlorine and total chlorine. Part 13: N, N-diethylphenylene-1,4-diamine titrimetric method
20.***ESRI (Environmental Systems Research Institute), 2015. ArcGIS 10.3.1 for Desktop Help.
21.KRIVORUCHKO. K., GRIBOV. A., KRAUSE. E.,Multivariate Areal Interpolation for Continuous and Count Data, Procedia Environmental Sciences, Volume 3: 14–19, 2011.
22.MITAS. L., MITASOVA. H., Computer and Mathematics with Applications. Vol. 16. No. 12. 1988, p. 983–992.
23.BĂLĂNICĂ. DRAGOMIR. M. C., SIMIONESCU., C.I. BICHESCU, MUNTENITA. C*, The assessment of using the sewage sludge in agriculture in Romania Mat. Plast. (Bucharest),**55**, no.4, 2018, p. 700-703

Manuscript received: 9.10.2019