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Tertiary Treatment of Livestock Wastewater in the Context of Alternative Water Resources for Sustainable Agriculture

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Abstract: *The limited availability and quality of water resources are key issues of water management, and the protection and preservation of water resources are a requirement in the context of accelerated economic growth and principles of sustainable development. The experimental research presented in this paper is based on the need to identify alternative water sources and support unconventional wastewater treatment methods which would enable their reuse in areas affected by water scarcity and drought. Livestock wastewater contain significant levels of nutrients (nitrogen and phosphorus) and may represent an attractive water source for crop irrigation. This paper evaluates the efficacy of a proposed technological process for tertiary wastewater treatment consisting of two steps: electrochemical treatment for the removal of suspended and colloidal impurities and ozone disinfection. The experimental results showed higher efficiencies for the removal of chemical pollutants (92.5% COD, 79.3% BOD, 98.6% TSS, 41% residue saline) and significant inactivation of microorganisms (over 99.9% for total coliform bacteria and in some cases 100% for faecal coliform bacteria and faecal streptococci). The quality of the effluent complies with the regulations for wastewater use in agriculture and allows its reuse for different categories of use considering the required conditions for soil/crops. The successful application of treated wastewater to agricultural crops depends in a high extent on the good practices aimed on the improvement of crop yield and quality, optimisation of soil productivity and protection of the environment undertaken by the economic entities.*

Keywords: *electrocogulation, ozone treatment, livestock wastewater*

1. Introduction

The main issues of water management should be considered in the broad context of a well-balanced social and economic development which would not compromise the sustainability of the ecosystems. [1,2]. Limited availability and water quality are key issues of water management and continued efforts are made for the protection and preservation of water resources by adopting adequate politics at administrative level. The current progress of scientific and academic research in the development of efficient wastewater treatment methods enables the reuse of treated effluent in various purposes [3-5].

The use of unconventional water sources such as treated wastewater is a compelling alternative particularly in areas affected by the lack of water resources and drought events [6-9]. Agriculture is among the economic sectors which require access to sufficient water resources and approx. 70% of global freshwater resources are used in agricultural purposes. Moreover, 28% of the global agricultural land and 56% of the total irrigated land are located in areas with high and very high water shortage [10].

Livestock wastewater has high contents of nitrogen and phosphorus which may be used as potential sources of nutrients for plants growth. For the reuse of such wastewater in crop irrigation, proper treatment should be employed to reduce the pollutants load. Potential effects on public health and adverse effects on soil and the environment should be considered as priority aspects for the successful development of projects involving wastewater reuse for irrigation. Also, a series of good practices regarding irrigation should be considered, particularly those depending on the local climatic conditions, soil physicochemical characteristics, crop selection, irrigation techniques, application rate of irrigation water etc. [11,12].

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National and international regulations prohibit the use of raw wastewater for crop irrigation and provide rules for its use based on the quality of the treated effluent in conjunction with the type of soil/plant [13,14].

Livestock wastewater has a complex and diverse composition, with high content of pathogens, organic substances (COD, BOD), nitrogen and phosphorus forms, suspended matter (TSS), salts. Toxic organic compounds such as pesticides and antibiotics are also present in this category of wastewater. From the health perspective, the main hazard associated with the use of insufficiently treated wastewater for crop irrigation is the presence of pathogens. As regards the effects on the environment, the main concern is related to the increase in soil salinity which may alter soil composition and leaching behaviour and may decrease the long-term soil productivity [15]. Although pesticides and antibiotics are found at low levels in wastewater, an incresed interest should be granted to them as they have a hazardous nature owing to their high persistence in the environment. The presence of antibiotics in soil may disturb the microbial communities and favour the evolution and spread of antibiotics resistance [16].

Usually, a local treatment of livestock wastewater is achieved by means of conventional systems consisting of a primary step for the mechanical separation of course matter and a secondary step for the aerobic or anaerobic biological treatment. Specific chemical and microbiological pollutants that cannot be removed by conventional methods need to be processed in an additional step, namely tertiary (advanced) treatment which enables the obtaining of an effluent with superior quality. Several processes were developed and used for the removal of pollutants considering the particularities of the treated wastewater [17-20].

Electrocoagulation is a wastewater treatment technique which enables the removal of organic and inorganic suspended matter by means of electro-generated iron or aluminium ions which facilitate the aggregation of particles. The metallic ions are generated by the passing of a current between two electrodes (a sacrifical anode and a cathode) immersed in water. These ions undergo hydrolysis and form species - mainly hydroxides - which act as coagulants. The coagulation process is usually followed by flocculation and sedimentation [21-24]. In contrast with conventional coagulation using aluminium or iron salts, electrocoagulation has the advantage that the generation of ions does not require addition of chemicals, generates low amounts of sludge and it is an easier and safer to use. The addition of salts would lead to increased salt content in the treated effluent, thus contributing to the increase of soil salinity and crop degradation. This reduces the volume of treated effluent to be used in irrigation purposes and makes mandatory its dilution prior to application on soil [13].

Equations 1-3 describe the main reaction taking place at the anode (aluminium or iron) and cathode [21, 22]:

Al anode: $$\mathrm{Al(s)} \rightarrow \mathrm{Al^{3+}(aq)} + 3e^- \quad (1)$$
Fe anode: $$\mathrm{Fe(s)} \rightarrow \mathrm{Fe^{n+}(aq)} + \mathrm{n^{e-}} \quad (2)$$
Cathode: $$\mathrm{2H_2O} + 2\mathrm{e^-} \rightarrow \mathrm{H_2} + \mathrm{2HO^-} \quad (3)$$

During electrocoagulation, secondary reactions may take place depending on the composition of wastewater and other compounds may be generated such as free chlorine, hypochlorite and other oxidizing reactive species [25].

The efficacy of the electrochemical process and the energy requirement are affected by a series of parameters. The most important ones are current density which influences the dose of generated coagulant, water pH which should be maintained at optimum values to ensure the generation of metallic ions, stirring rate, temperature, number of electrode pairs, size and distance between the electrodes [26]. Among the drawbacks of electrocoagulation, the passivation and dissolution of electrodes are to be mentioned, as they impose the regular cleaning and replacement of the electrodes.

Ozonization is a wastewater treatment technique which employs ozone for the advanced oxidation of organic matter. Ozone has high oxidation potential and reactivity and has been proven efficient in the removal of organic compounds otherwise hardly degradable by conventional processes, such as pharmaceuticals and pesticides [27,28]. Ozone is also a very efficient disinfectant enabling the inactivation of bacteria, viruses and some protozoa, including pathogens that are usually resistant to other chemical disinfectants (e.g. chlorine, chloramine, hydrogen peroxide etc.). The efficiency of ozonation depends on the ozone dose, contacting time and wastewater characteristics [29,30]. Major changes of water colour and odour removal have been attributed to ozonation leading to a better acceptability of the public against the reuse of treated effluents in agricultural purposes [31].

This paper presents the application of a technological procedure for the tertiary treatment of livestock wastewater by chemical means. This procedure reduces the pollutants up to levels that enable the adequate reuse of the treated effluent for various crop irrigation purposes.

The investigated procedure consists of two steps: the removal of suspended matter and colloids by electrocoagulation using aluminium electrodes and the advanced oxidation of organic matter and disinfection using ozone.

2. Materials and methods

The experimental investigations were conducted at laboratory scale on wastewater resulting from a medium sized dairy farm. The wastewater was previously subjected to on-site wastewater treatment in a biological pond. Thus, some gravitational separation of suspended matter and decomposition of organic matter by aerobic-anaerobic processes was already achieved prior to the experiments. However, this effluent did not achieve the adequate quality parameters to be used in agricultural purposes and additional treatment is compulsory.

The laboratory setup consists of two modules for the advanced treatment of livestock wastewater. The coupling of electrocoagulation and ozonisation technologies was based on their mutual synergistic benefits toward greater removal efficiencies of anthropic pollutants [32, 33]. Because the classical coagulation technique would add even more salts to the treated wastewater, the anodic introduction of aluminium ions through electrocoagulation was preferred [34]. The electrocoagulation module (EC) consists of a cell provided with 2 aluminium electrodes connected to a direct constant current power supply, with the distance between the electrodes being kept at 5 mm, their polarities being reversed each minute. The electrochemical cell has a rectangular shape, with vertical water flow (Figure 1-a). The electrochemical process was conducted in dynamic regime, with constant flowrate of 4 L/h. The cell was operated at constant current density of 100 A/m^2, providing a peak dose of approx. 300 mg Al(III)/L depending of the quality parameters of wastewater. The dispersion of aluminium ions in the water volume was achieved by means of a hydrodynamic stirring system. The electrochemical setup was based on general recommendations as regards the practical distance between the electrodes and the general required current density to avoid most secondary problems derived from too low or too high values [35, 36]. Wastewater was collected in a homogenization tank and the aggregation of flocs was achieved by adding a dose of 10 mg/L of a cationic polyelectrolite Floerger followed by the slow stirring at 40 rpm for 10 min. The chemical sludge was separated by gravitational sedimentation for 120 min. The flocculation parameters were set through jar test optimisations on the processed wastewater [37,38].

The second module is dedicated to the ozonization process and uses as input the effluent resulting from the electrocoagulation module. The ozone treatment employs 3 work units, as follows (Figure 1-b):

- unit for ozone generation;
- ozonization reactor;
- unit for the retention of unreacted ozone.

The unit for ozone generation provides the reaction gas by ionising the oxygen from air using Corona-type electric discharges. The flowrate of ozone was 4.2 g/h determined by the iodometric method in the experimental setup. The ozonization reactor is column type (H = 1 m) provided with sparger to enhance the transfer of gas to the liquid phase. The ozone treatment was conducted in stationary regime and the treated volume was 3 L. The unit for the retention of unreacted ozone is meant to retain the excess ozone and prevent its evacuation in the atmosphere, as it is a toxic and irritant gas. This unit consists of two absorption columns with granular activated carbon and two columns with indicator solution (c = 10 mg KI/L).

The determination of wastewater quality indicators was performed using standardised analysis methods, using conventional and instrumental methods, as follows: pH (ISO 10523:2009), turbidity (EN ISO 7027-1:2016), electrical conductivity (EN 27888:1997), total suspended matter (EN 872:2005), COD (ISO 6060:1996), BOD (EN 1899:2003), phenols (ISO 6439:2001), nitrogen (ISO 10048:2001), phosphorus (EN ISO 6878:2005), aluminum (EN ISO 12020:2004), total and faecal coliform bacteria (ISO 9308-2:1990), faecal streptococci (EN ISO 7899-2:2002), antibiotics (EPA 1694:2007, UHPLC on-line SPE Thermo Scientific E Quan MAX Plus LC-MS / MS TSQ Quantiva).

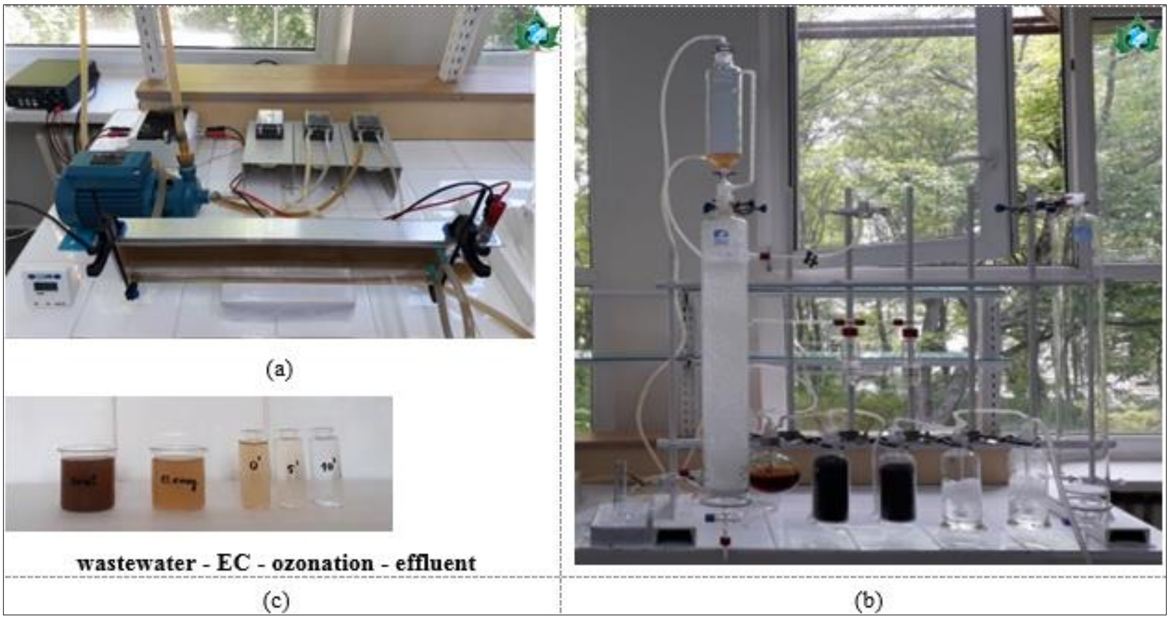

Figure 1. Experimental set-up for the advanced (tertiary) wastewater treatment:
(a) electrocoagulation step ; (b) ozonation step ; (c) the variation of colour of treated wastewater

3. Results and discussions

In order to achieve the aim of this paper, the physicochemical and microbiological profile of the wastewater subjected to advanced treatment was investigated. Table 1 presents the quality parameters of interest in relation to the reuse of wastewater for crop irrigation. The allowable concentrations as provided by the national (STAS 9450:1988) and international (ISO 16075:2015) regulatory documents are also presented. The quality of the wastewater was assessed considering the indicators provided by the regulations concerning water reuse in irrigation purposes (biochemical oxygen demand, total suspended matter, aluminiu, conductivity, saline residue, total coliform bacteria, faecal coliform bacteria) together with some other indicators of interest for wastewater (*p*H, turbidity, colour, chemical oxygen demand, phenols, nitrogen and phosphorus content, faecal streptococci).

Table 1. Quality of (pretreated) livestock wastewater

Quality parameter	**Unit**	**Value**	**Allowable concentration (ISO 16075:2015)**		**Allowable concentration (STAS 9450-88)**
			Category C	***Category D***	
Colour	-	brown	N/A	N/A	N/A
pH	pH units	7.1	N/A	N/A	N/A
Turbidity	NTU	286	N/A	N/A	N/A
Electrical conductivity	mS/cm	4.3	N/A	N/A	2.25 (C3) 5 (C4)
Total suspended matter	mg/L	207	50	140	N/A
COD	mg/L	1,351	N/A	N/A	N/A
BOD	mg/L	126	35	100	N/A

Phenols	mg/L	0.18	N/A	N/A	N/A
Nitrogen	mg/L	232	N/A	N/A	N/A
Phosphorus	mg/L	45	N/A	N/A	N/A
Residue saline	mg/L	2,481	1,500 (C3) 3,250 (C4)	N/A	N/A
Aluminium	mg/L	0.17	N/A	N/A	5 (high irrigation) 20 (low irrigation)
Total coliform bacteria	no/1000 mL	5,420,000	N/A	N/A	100 (M1) 100-100,000 (M2) 100,000-1,000,000 (M3)
Faecal coliform bacteria	no/1000 mL	1,410,000	100,000	N/A	absent (M1) 10,000 (M2) 10,000-1,000,000 (M3)
Faecal streptococci	no/1000 mL	400,000	N/A	N/A	N/A

Note: Saline residue = $Na^+ + Ca^{2+} + Mg^{2+} + Cl^- + SO_4^{2-} + HCO_3^- + CO_3^{2-}$
M1 – all types of soils and plants; M2 – all soils and plants except highly permeable soils and food and feed plants, without heat treatment; M3 - lands with groundwater at more than 4m depth and heat-treated crops, as well as non-food vegetables;
C3 – high saline residue - usable with special arrangements for washing and drainage, on permeable soils and salinity tolerant plants; C4 - very high saline residue - usable with special arrangements for washing and drainage, on permeable soils and in plants very tolerant to salinity.

The values of wastewater quality parameters are discussed in relation to the recommendations provided by national (STAS 9450:1988) and international (ISO 16075:2015) regulatory documents in order to prevent the issues generated by the use of improper reclaimed water.

The results showed a relatively low percentage of biodegradable organic compounds (BOD) related to the total content of organic substances (COD) from wastewater. This is due to the oxidation of organic matter during the long-term biological treatment in the pond. Nevertheless, the most permissive limit for BOD value is 100 mg/L and corresponds to the restricted irrigation of *industrial and seeded crops* (category D), while the limit value for BOD for the use of reclaimed water in *agricultural irrigation of processed food* (category C) is 20 mg/L. Another quality indicator used to establish the irrigation purpose for treated wastewater is the content of suspended matter (TSS – total suspended solids). In this case, the most permissive limit is 140 mg/L and corresponds to the restricted irrigation of *industrial and seeded crops*, while the limit for the *agricultural irrigation of processed food* is 25 mg/L. Another aspect to be considered is the salinity of wastewater as it restricts the volume of reclaimed wastewater to be applied on soil. In this regard, the investigated livestock wastewater has high salinity (saline residue class C3). Also, the selection of irrigation purpose must consider the microbiological load of the reclaimed wastewater. For the investigated wastewater, the results showed a high bacteriological contamination (10^6 - 10^7). The mentioned regulations provide a limit of 10.000 no/1000 mL of faecal coliform bacteria for reclaimed wastewater used in *agricultural irrigation of processed food*.

The analysis of the behaviour of investigated livestock wastewater to the applied advanced treatment process was achieved by means of removal efficiency for specific pollutants in conjunction to process dynamic and observations on the changes of organoleptic properties of the effluents.

During the advanced treatment experiments, significant changes of turbidity was observed, together with the rapid discolouring of wastewater and removal of the unpleasant specific odour (Figure 1c).

As shown in Figures 2, the electrochemical treatment provided a significant reduction of organic substances (80.1% COD, 71.2% BOD) and suspended matter (88.4% TSS). The insertion of an electrocoagulation unit prior to the ozonization step was supported by literature reports showing that the efficiency of ozone disinfection is inhibited by suspended solids and colloids and their removal prior to ozonization is recommended [11]. Moreover, the removal of suspended matter reduces significantly the values of microbiological indicators as they tend to adhere to various solid substrates and substances present in water (Figure 3).

Another class of pollutants removed through electrocoagulation are salts and in this regard, a successful reduction of 40.6% of the saline residue was achieved. Thus the treated effluent may be included in salinity class C2, which allows its use for the irrigation of permeable soils and of plants moderately tolerant to salinity. The aluminium content from wastewater increased from 0.17 mg/L to 1.27 mg/L, however this value complies with the maximum allowable value of 5 mg/L as provided by the regulations.

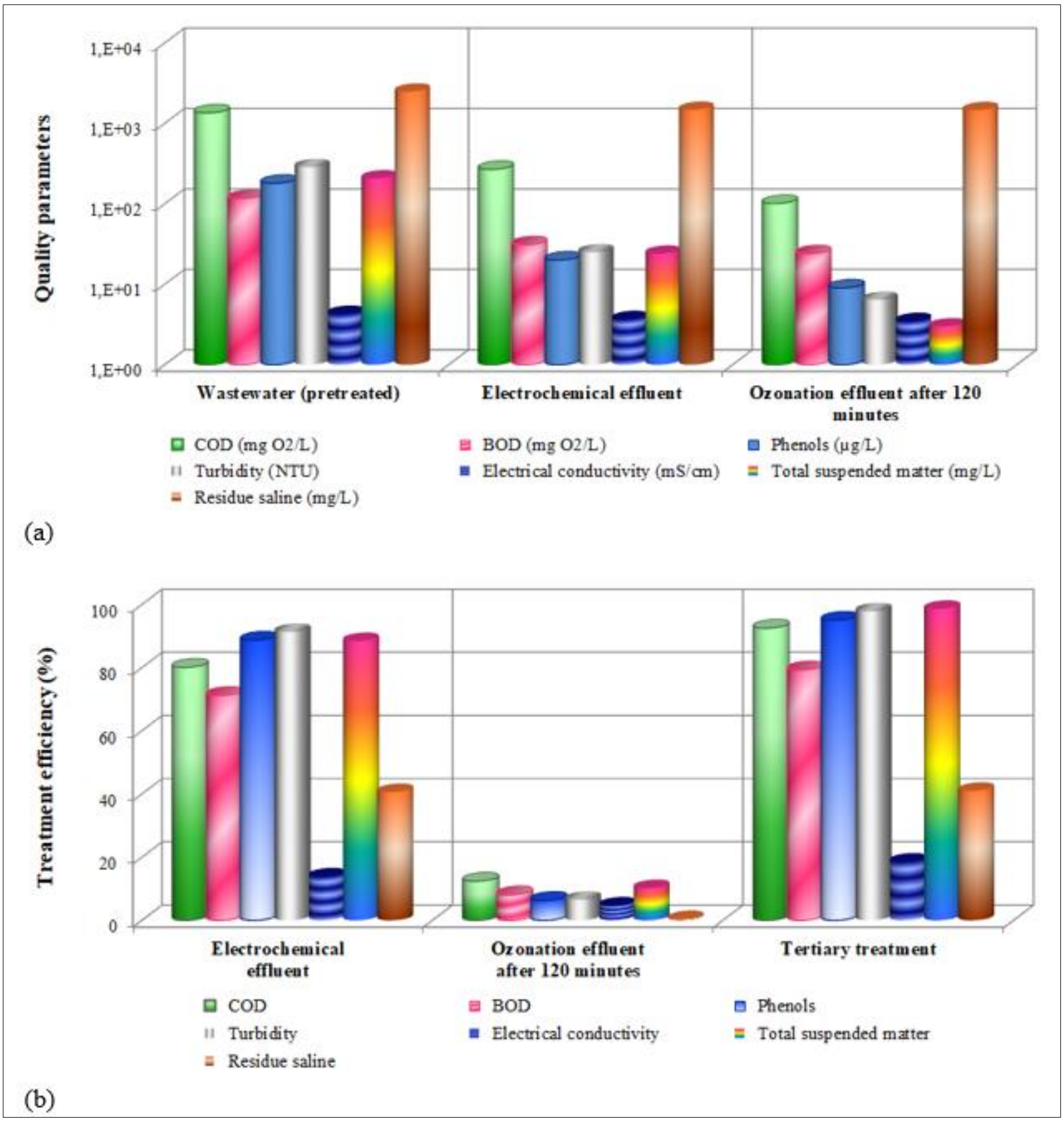

Figure 2. Removal of organic substances, suspended matter and salts from wastewater
(a) Variation of pollutant during wastewater treatment
(b) Efficiencies of pollutant removal

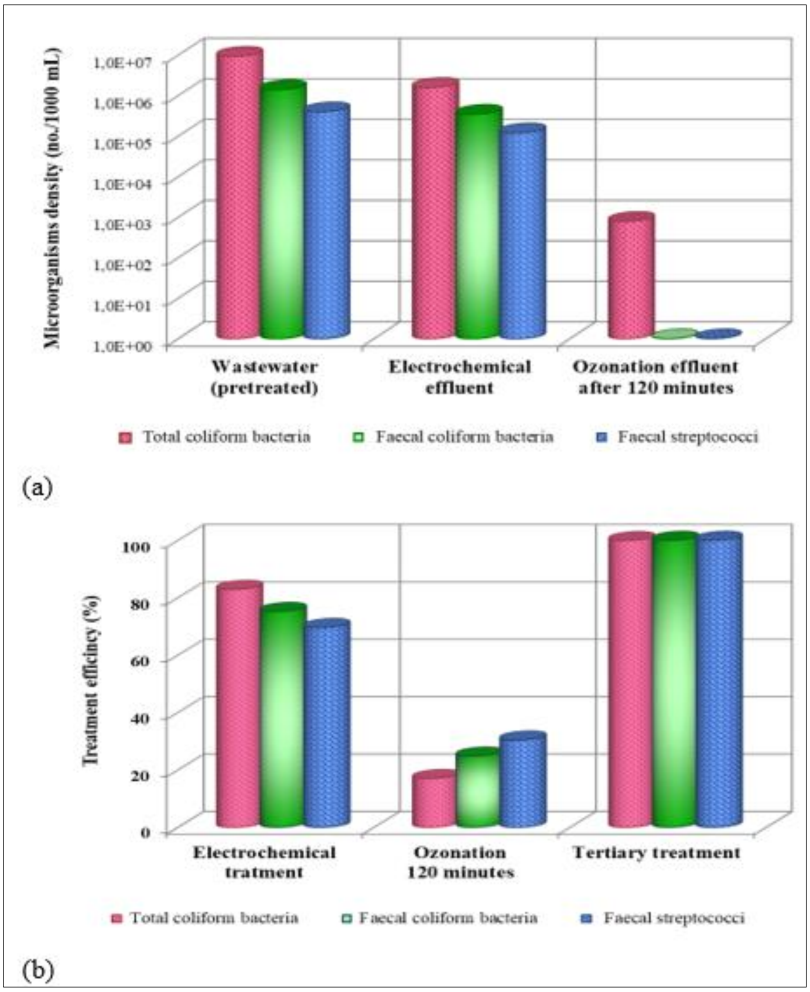

Figure 3. Removal of mciroorganisms from wastewater
(a) Variation of microbiological indicators during wastewater treatment
(b) Efficiencies of microorganisms removal

The subsequent treatment step consisted of advanced oxidation of organic matter using ozone and the results are depicted in Figures 2-3. The degradation of refractory organic compounds was achieved (12.4% COD, 8.4% BOD) together with the conversion of ammonium and nitrites ions to nitrates. For observing the degradation of antibiotics during ozonation, the spiking of wastewater with two antibiotics (ampicillin and gentamicin) was conducted. A known quantity of each antibiotic (1 mg/L) was added to the wastewater and the results proved their degradation up to ultra trace levels. As regards the disinfecting effect of ozone, the results showed good antimicrobial efficacy in the removal of bacteriological indicators, with removal efficiencies over 99.9% and in some cases 100% for faecal coliform bacteria and faecal streptococci (Figure 4).

Figure 4. The effect of ozone treatment on faecal coliform bacteria and faecal streptococci
Left - positive yellow test tubes with bacterial growth
Right - negative purple test tubes without bacterial growth

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4. Conclusions

This paper addressed a current issue related to water management, namely the adequate treatment of wastewater in relation to the necessity to identify alternative water sources in areas with water scarcity and prevent environmental pollution.

Livestock wastewater has high content of nitrogen and phosphorus forms which may be regarded as potential sources of nutrients for the plants. The presence of nutrients in wastewater is advantageous as it can help reduce the use of fertilizers, however the content of nutrients does not ensure entirely crop requirements and often they are present in forms that are not readily available for plants. Therefore, good fertirrigation practices should be employed to prevent the potential negative impacts (such as increase of soil salinity or nitrate leakage in groundwater).

The tertiary treatment solution consisting of electrocoagulation followed by advanced oxidation and disinfection with ozone ensures an effluent for reuse in agriculture adequate to the requirements of the final users. The proposed treatment process enhanced the removal of chemical pollutants from wastewater (92.5% COD, 79.3% BOD, 98.6% TSS, 41% residue saline) and inactivated significantly the microorganisms (over 99.9% for total coliform bacteria and in some cases 100% for faecal coliform bacteria and faecal streptococci). This ensured effluent parameters according to the limits provided for the irrigation of agricultural crops considering the type of soil/crops specified in the existing national (STAS 9450:1988) and international (ISO 16075-2:2015) regulations.

The setup of the technological solution proposed for the tertiary treatment of livestock wastewater has a series of advantages deriving from the fact that:

- the coagulation of suspended and colloidal matter using aluminium is achieved by an electrochemical process which, in contrast to the classical coagulation using aluminium sulphate, prevents the use of chemical compounds that contribute to the salt content of the effluent;
- the suspended and dissolved inorganic substances (saline residue) from livestock wastewater that cannot be removed by the conventional treatment technologies are reduced by means of electro-coagulation;
- it ensures the degradation of persistent organic pollutants such as antibiotics and pesticides hardly degradable by means of conventional treatment methods currently employed for livestock wastewater.

The investigated technological process is flexible, allows a fast start of the treatment and the modules may be operated as single units or in conjunction, depending on the specific treatment requirements.

The solution provided for the tertiary treatment of livestock wastewater enables prevention and mitigation of pollution and supports the economic agents in their efforts to identify alternative water sources and recover the useful substances, in accordance with the principles of a sustainable agriculture.

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