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ASPECTS OF IMPLEMENTATION OF MODERN TECHNOLOGIES IN ADVANCED WASTEWATER TREATMENT

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Abstract: The main objectives of waters and aquatic environmental protection aim preventing the damage of all surface waters and progressive reduction of pollution, gradual cessation or elimination of evacuation and loss of pollutants in the surface waters, as preventing or eliminating the contribution of pollutants in underground waters and preventing the damage of their.Gratifying water requests, protection of the aquatic environment and capitalization of their potential supposes the realization of the proper legislative frame and establishing the institutional framework, the implementation of legal provisions, realising necessary investments, as well as maintenance and exploitation of works.A special importance for water resources protection is the correspondent management of used waters by their purification to a degree that is correspondent to the present requirements of the national and European legislation, so that their overflowing in outlets not to produce ecological lacks of equilibrium or modification of water quality.In this work was done an assessment of the current state of wastewater treatment in Gorj county and were given new technology, modern, clean the advanced treatment of wastewater, to implement legal provisions in the field of water protection.

1. INTRODUCTION

Romania's water resources are made of surface waters – internal rivers, natural and artificial lakes, Danube River and underground waters. Romania is relatively poor regarding water resources, having only 1870 m^3 of water per inhabitant and year in Europe. Due to interactions hydrosphere – atmosphere – lithosphere – living organisms, natural water is never chemically pure. In the chemical composition of natural waters enters a series of substances, namely: dissolved gases (O_2, N_2, CO_2, SO_2) coming mainly from atmosphere with which water is in contact or from chemical reactions that take place in the water; organic or inorganic compounds in suspension, like: vegetal rests, microorganisms, mineral dusts, sand, etc.; variable quantities of chemical combinations (organic and inorganic) made mainly of dissolved salts, that are in aqueous solution or having the form of ions. From the point of view of natural chemical composition of the surface waters, at least two processes must be taken into consideration: water interactions with the atmosphere and water interaction with minerals and rocks [1].

At the interface water – atmosphere, rains wash foreign particles from the atmosphere: gases (N_2, NO_2, NH_3, SO_2, H_2S, CO_2), mineral and organic dusts that are in suspension, etc and introduce them in the surface waters.

At the second interface (water – lithosphere), minerals and rocks dissolution by waters depends on several factors, like: rocks and mineral's nature, contact surface (aggregate grading and rock's porosity), contact time and temperature [2].

The main objectives of water and aquatic environmental protection aim:

- preventing the damage of all surface water bodies;
- protection, improvement and reconstruction of all surface water bodies with the purpose of reaching their good status, up to 22 December 2015;
- progressive reduction of pollution that is due to foreground substances and gradual cessation or elimination of evacuation and loss of substances that are foreground dangerous;
- preventing or eliminating the contribution of pollutants in underground water and preventing the damage of the status of all underground water bodies;

- reversing any significant and sustainable attempt to increase the concentration of each pollutant that results from the impact of human activity, to reduce in a significant manner underground water pollution.

Integrated management of water resources represents a practical modality for the application of the concept of sustainable development in water fields. By applying the principles of integrated management it is promoted the development and coordination of water, of the fields and their resources, for the optimization, social and economic equilibrated development not compromising the durability of ecosystems [3,4].

Integrated management of water resources supposes:

- integration of the system of water natural resources;
- integration of management infrastructure of water resources in the natural capital;
- integration of water usage;
- integration upstream – downstream;
- integration of water resources in planning politics.

The European Legislation in the field of water resources protection covered three stages:

- first stage (1975-1980) – *Protection of water use* – having as objective to establish some quality standards of the environment defining specific limits for water resources that are used for the production of potable water and for water usages;

- second stage (1981-2000) – *Pollution reduction in the source* – through which it was aimed the establishment of some limit values admissible by exhaustion of polluters in the aquatic environment;

- third stage (after 2000) – *Waters sustainable management* – to ensure reaching a “good” status of all water bodies from the European space, to ensure some similar life conditions from the point of view of the aquatic environment for all citizens.

One of the European directives in water field, having as limited period of implementation the 31.12.2018 is the Directive no. 91/271/EEC regarding the purification of urban used waters. The objective of the directive is represented by the protection of the environment against negative effects of exhausted city waters from certain industrial fields (especially food industry). This directive have been transposed in Romanian legislation by HG 188/2002 for the approval of some norms regarding conditions of unloading in the aquatic environment the used waters.

2. EVALUATION OF THE ACTUAL STATUS OF SURFACE WATERS FROM GORJ COUNTY AND TECHNOLOGIES OF WATER ADVANCED PURIFICATION

2.1. THE ACTUAL STATUS OF SURFACE WATERS FROM GORJ COUNTY

In Gorj county, the main fields of activity from which used waters come are: electricity and thermal energy production, coal extraction, extraction of petroleum and gas, industry of construction materials, chemical industry, zoo technical units and communal household.

Regarding the extent to which have been fulfilled the requirements of the Directive 91/271/CEE, from the information contained in the environmental report of the Agency for Environmental Protection Gorj, at the level of year 2009, can be obtained the following conclusions:

- the gravity of sufficiently purified waters represented more than 54% as can be seen from Fig.1.

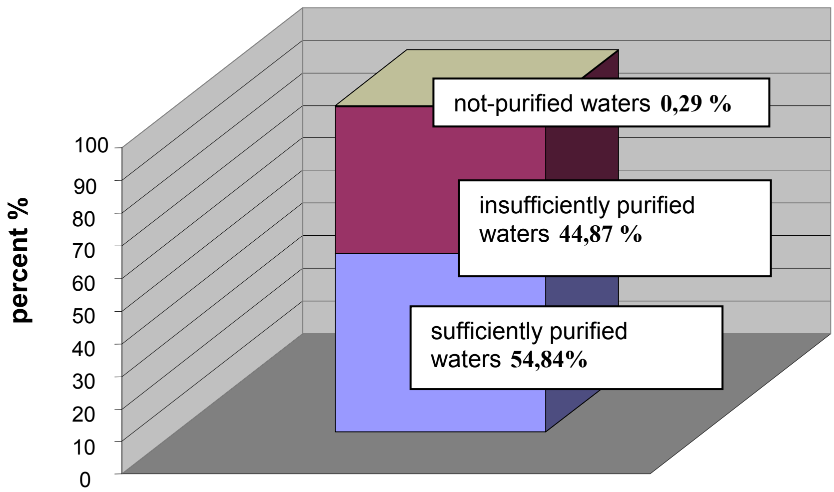

Fig.1 The gravity of sufficiently/insufficiently purified waters in Gorj county.

- the gravity of used waters on segments of activity is presented in Fig.2 from which it can be seen that the energetic and mining sector is the one that contributes in a significant manner to the total volume of used water at the level of the district.

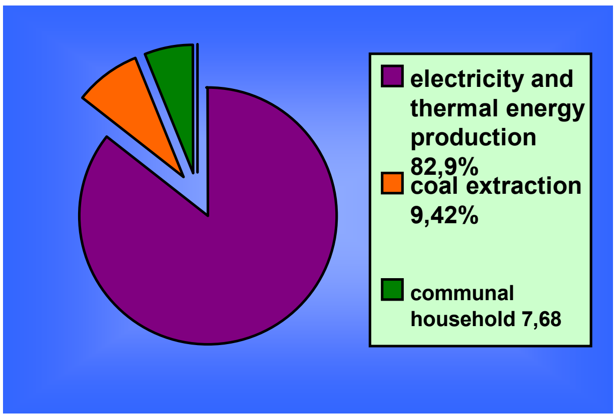

Fig.2. The gravity of used waters on segments of activity.

Discussing about the sewerage net that exists in Gorj county, this has a length of 184,2 km, the greatest part being in the urban area, in the rural area being only 9 km of sewerage net. Gathering used waters at the sewerage net is realised in 13 localities (9 towns and 4 communes). There are numerous localities and streets that, even if they have networks of water distribution, they do not have sewerage networks, the domestic used waters reaching directly the soil. Also, there are provided works of aggrandizement, modernization and rehabilitation of existent networks, namely construction of new networks to gather used waters.

The following localities in Gorj county have town/ communal purification stations:

- Municipality of Tg. Jiu has a purification station that has a mechanical and biological stage; designed for a debit of 500l/s; biodegradable organic loading (CBO_5) of 200 mg O_2/l; suspensions concentrations of 200 mg/l.

The analyses made on the effluent exiting the purification station presents transgressions at the indicators: CBO_5, NH_4^+, BCT, BCF.

- Municipality of Motru has a purification station that is provided with mechanical and biological stage, having a capacity of 5000 mc/h. Exhausted used waters are not purified in a correspondent manner, presenting exceeding of the admitted limits at the indicators: NH_4^+, BCT, BCF, CBO_5.

- Rovinari City does not have a purification station. The waters that are evacuated in river Jiu does not present exceeding of the limits admitted at the indicators: suspensions, CBO_5, NH_4^+.

2.2. PURIFICATION TECHNOLOGIES BY OXIDATIVE DEGRADATION OF POLLUTING SUBSTANCES IN THE WATER

The chemical oxidation is applied normally when residual water contains contaminants which are not easily biodegradable, or are not biodegradable at all (for example inorganic component) which can misadjust the physical – chemical process or the biological one as part of the purification station or are having properties that are too harmful to allow them the release in the common sewerage system. Examples of such contaminators are: oils and lubricants, phenols, aromatic polycyclic hydrocarbons (PAH), colouring agents, pesticides, cyanide, sulphurs, sulphite, complexes of hard metals etc.

Some of these contaminants are biodegradable to a certain extent and can be treated in an alternative manner with microorganisms that are specially adapted in this sense. In these cases, it depends on the situations at local level if chemical oxidation or the biological one is preferred. When small quantities of residual water are involved or when there is no available bio treatment as part of the location, the chemical oxidation might be a recommended method for treatment instead of installing a stage of biological purification.

The reactions of oxidation with active oxygen (ozone, oxygenated water), most of times accompanied by irradiation with UV rays, are used, for example, for the treatment of leach discharge from fields or for alienating the refractory CODE, smelling components or pigments [5,7].

The oxidation with the aid of chlorine or sodium chlorite might be used in certain conditions for alienation of the organic contaminants, an example this way is the SOLOX® process through which is eliminated (at increased temperatures and pressures) COD/TOC and AOX from the residual water as a result of epichlorohydrin. But using chlorine, hypochlorite, chlorite (or those halogenated compounds) must be applied with precaution in each case, due to the risk of generating organic halogens from the organic content of the flux of residual water, having cancerigenous effects.

Supercritical oxidation in water (SCWO) is a special application of the variant with increased pressure of the air oxidation. The oxidation reaction takes place in the overcritical are of the water, namely at temperatures above 374 °C and pressures over 22,1 MPa. The process is presented in Fig. 3.

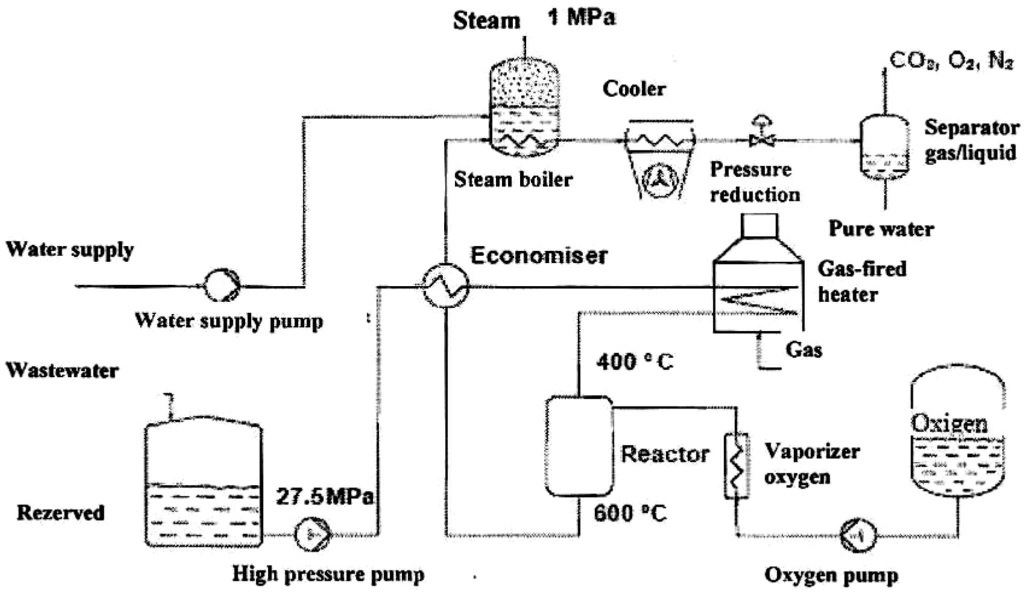

Fig.3. Installation of water purification through supercritical oxidation.

The residual water is brought at the supercritical pressure with the aid of a pump under increased pressure, before entering the economizer, where the supply is preheated by the effluent of the reactor. While starting or if the organic concentration from the residual water is smaller than 4%, the supply must be heated continuously to reach the supercritical temperature interval. When oxygen is added for supply, the temperature from the reactor increases to about 600°C. The effluent of the reactor drains to economizer, afterwards passes through a steam generator with heat recovery and through a device for cooling the effluent. At the end, a control valve decreases the pressure of the effluent in the atmospheric conditions, and the liquid and gases are separated.
The organic content from the residual water is reduced at the carbon dioxide, water and azoth. SCWO characteristics are: complete solubility of organic compounds in supercritical water; complete precipitation of inorganic solids, like salts; necessary reaction periods for complete destructions are positioned between 30 and 60 seconds, depending much on the reaction temperature; reaction is realised at about 25MPa and at 400-600°C; complete transformation of organic content (organic carbon is transformed in carbon dioxide, organic and inorganic azoth is transformed in azoth having gas form, organic and inorganic halogens are transformed in correspondent acid, organic and inorganic sulphur is transformed in sulphuric acid); destruction of volatile solids; oxidation of hard metals up to their most increased oxidation status.
SCWO applies to all contaminated agents having a low biodegradability and/ or a high toxicity, as part of chemical, petrochemical and pharmaceutical industry. Destroys also the dioxides and PCB (biphenyl polychlorinated), meanwhile the temperature interval is low 400-600°C makes improbable the production of NOx (namely, azoth oxides, excluding N_2O). Another field of application of the SCWO is industrial and municipal slime treatment to destroy toxic organic compounds, including dioxins.

METHOD OF ELECTROCHEMICAL OXIDATION OF CYANIDES IN RESIDUAL WATERS

Regarding the electrochemical oxidation of cyanides in residual waters, a great importance is held by electing the material of which is confectioned the anode, the basic condition being its insolubility in the oxidation process. As a result of the oxidations realised with anodes made of plum, nickel, stainless steel, magnetite, graphite, it was reached the conclusion that the best anodes are the ones in graphite or magnetite. Their lack of advantage resides in the granulometric degradation of graphite and hard processing of the magnetite [6].

The electrochemical oxidation on anode appears according to the reaction:

$$CN^{-} + 2OH^{-} 2e^{-} \longrightarrow CNO^{-} + H_2O \qquad (1)$$

For the electro-chemical oxidation of the cyanides on platinum anode, at the beginning takes place the oxidation of free CN ion, which is very instable and passes in stable firm with cyanates formation. The cyanates that are formed, will be oxidised up to elementary azoth and carbon dioxide:

$$2CNO^{-} + HO^{-} - \ 6e^{-} \longrightarrow N_2 + 2CO_2 + 2H_2O \qquad (2)$$

Simultaneously takes place the unloading of the hidroxilic ions:

$$4OH^{-} 4e^{-} \longrightarrow 2H_2O + O_2 \qquad (3)$$

The oxidation speed of the cyanides can increase to a considerable level, adding in the treated solution, sodium chloride. The technological scheme of an industrial installation for the electrochemical purification of residual waters with cyan content is represented in Fig. 4.

Using the method is adequate for neutralization of residual waters which are formed due to multiple usage of water in industry and which contain cyanides in increased concentrations. The functioning of the installations is completely automatic and applied in many countries with mining industry of developed profile.

Electrochemical oxidation is a procedure which can be applied for waters having a high content of cyanide (150-230 mg/l). The disadvantage of the method resides in the fact that it cannot be applied but for small quantities of water, of only several m/h. The installations that are used in the electrochemical oxidation are completely automatic, which allows a rigorous control and a maximum efficiency in the application of such a procedure.

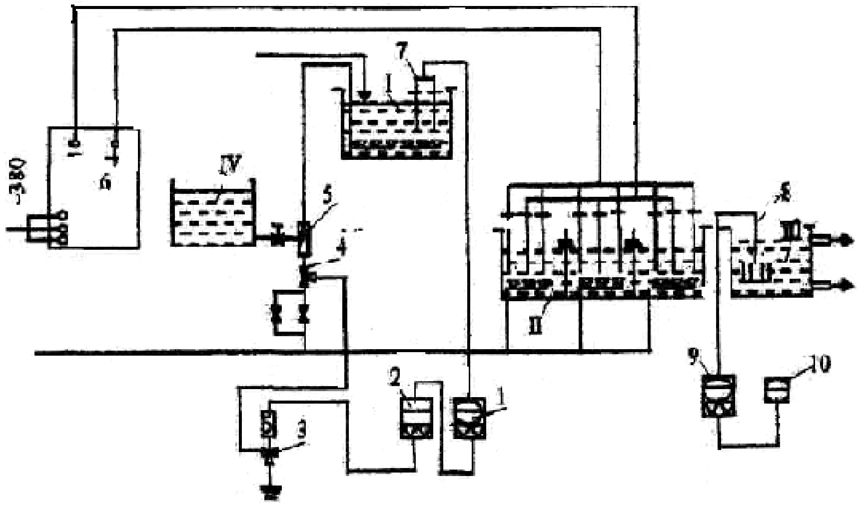

Fig. 4. Installation for the electrochemical oxidation of cyans.
I - reservoir - accumulator; II - electrolyser; III – reception vase; IV -reservoir for solution of sodium chloride; 1, 2, 7 – measuring device, regulator and transducer of the conductometer; 3 - electro-pneumatic transformer; 4 – pneumatic valve; 5 - ejector; 6 – alternative electricity rectifier; 8, 9, 10 – transducer and registers to measure remaining cyanides concentration.

Knowing, experimenting and implementation of some procedures for the elimination of pollutions from cyanic waters is of a great importance in the field of environment protection, taking into account the great toxicity of cyanic pollutants for aquatic environments and the especially difficult consequences of their presence, even in very reduced quantities, in the composition of the effluents.

3. CONCLUSIONS

The quality of surface waters in Gorj county is influenced by the industrial activities of exploitation and processing the natural reserves, without respecting the ecological restrictions, the wastes resulted from different activities realised on the territory of the district, having a polluting character. At the present moment there are realised numerous efforts to maintain and improve the water's quality. It develops and there appear numerous and varied technologies for the purification of used waters that, in the end, have as purpose the protection of water quality. Even this way, the measures of water protection proves to be insufficient, in some cases, these are left behind in respect to the rhythm of increasing waters pollution. Water management must have as main directions:

- The development of some projects regarding the rehabilitation and modernization of the water networks financed either from local budgets or through European programs;
- The development and accreditation of some methods for the analyze of the dangerous substances/ mainly dangerous, settled by the present environmental legislation;
- Issuing some new technologies of purification of the industrial and town residual waters
- Issuing some technologies of recovery/ capitalization of the useful substances from residual and town waters.

Water management is considered as being an inter-sectors problem, with an important role in all fields: health, alimentation, security, transport, commerce, etc. In this context, the integration of the management systems in all development politics is essential.

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