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Full Length Research Paper

Effective methods for potable water depollution in Vatra Dornei area, aiming the biodiversity and environmental protection

[1]Simona Ivana, [2]Octavian Ionescu, [3]Zoran Constantinescu, [4]George Goran, [4]Elena Rotaru, [5]Delia Costache, [5]Cristea Costache

[1]Center of Mountain Economy (CE-MONT), National Institute for Economic Research "Costin C. Kiritescu", Romanian Academy, 13 Septembrie 13 Street, 050711, Bucharest, Romania
[2]INCD IMT National Institute for Research and Development in Microtechnologies, 126A, ErouIancu Nicolae Street, 077190, Bucharest, ROMANIA
[3]UPG Petroleum and Gas University of Ploiesti,39Bucureşti Street, 100680, Ploieşti, Romania
[4]Faculty of Veterinary Medicine, University of Agronomical Science and Veterinary Medicine of Bucharest, 105 SplaiulIndependentei Street, 050097, Bucharest, Romania
[5]Transilvania University of Brașov, Faculty of Medicine, 29 Eroilor Street, 500036, Brașov, Romania

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The Center of Mountain Economy (CE-MONT), is located in Vatra Dornei in Romanian mountain area. Vatra Dornei city is placed at the confluence of Bistrita Aurie and Dorna rivers on the so called Dornei or Depression. This paper has the goal of presenting some innovative methods which could be used for depollution of potable water if some unpredictable events occur. The aim of our experienced research team is to active participate in population, biodiversity and environment protection through the design and production of a technology and an autonomous, long life, and effective equipment for water depollution.

Keywords: nanofilters, microbial fuel cells, biosensor, system water, safety, processing foods, lifespan.

INTRODUCTION

The beauty of Vatra Dornei landscape, the mineral and thermal water, the unique climate and its skiing resort are factors which made off this city one of the well-known touristic attraction of Romania. Although this city has a population of about 14429 inhabitants, the increasing number of tourists is creating a certain pressure on the potable water delivery.

The potable water source for Vatra Dornei city is mainly the Dorna River. It could be noticed that accidents may occur and randomly could happened that small quantities of organic fertilizers from small farms or residual water from mineral water bottling plants could affect the quality of Dorna river water.

This paper has the goal of presenting some innovative methods which could be used for depollution of potable water

*Corresponding Author's Email: simonaivana@yahoo.com

if some unpredictable events occur. The aim of our experienced research team is to active participate in population, biodiversity and environment protection through the design and production of a technology and an autonomous, long life, and effective equipment for water depollution. The designed equipment shall be also low cost in order to become accessible for small communities thus providing a real impact both on the economic and social life of community and on the available water sources.

The Center of Mountain Economy (CE-MONT), is located in this Romanian mountain area. It has 12 research laboratories, a conference hall with 200 seats, a library, a small printing press, and 2 mobile laboratories for field work. The CE-MONT goal is to foster regional cooperation and become "a pole of excellence" for the Carpathian-Balkan mountain area.

Another goal of this article is to emphasize the importance and necessity of the development and implementation of reliable, low cost monitoring systems for the potable water and furthermore for the rivers which provide water for wildlife.

Through an active monitoring of water in this region, pollution, animal infections or any other diseases would be detected in real time and thus undesirable events with serious economic and social impact will be avoided.

A solid background for this study is provided by the patent: RO 127171, „Composite, biodegradable, poly-functionalized material and process of manufacturing it" which brings to the society a new biodegradable material capable to reduce oxidized contaminants such as (nitrites, perchlorates etc.), and destroy, separate, encapsulate biological contaminants from surface water.

The scope of this paper is to create a filtering and monitoring device for contaminated water, from, but not limited to, residential waters (fountains, lakes, rivers). This article addresses the problem raised by UNESCO while studying the development of drinking water sources around the world through the World Water Development Report 2003, which observed a decrease in drinking water availability, achieving a drop of 30 to 40% in 2023.

The objective of this study is to create the device in a cost effective manner, making it accessible to small communities, to make it autonomous and with a sufficient lifespan, thus becoming a viable product both economic and social, through its impact on drinking water sources at community level.

Moreover, according to an OKO funded study, in 2021, Romania has 91% drinking approved water sources at urban level and 16% at rural level. In this context, we considers a priority the development of such a cost effective, autonomous devices, capable of active monitoring of water community water sources, especially used for animals. By active monitoring the water, animal infections could be detected in real time, with both economic and human health consequences, but also actively cleaning the water supplies and preventing imminent dangers. Using as a starting point the RO 127171 Romanian patent, which details a composite material, poly-functionalized, biodegradable, capable of separating, encapsulating and completely degrading biological contaminants and their metabolites, available in surface waters, together with a system of tubular microbial fuel cells (MFC) active in the reduction of oxidized contaminants (nitrates, perchlorates, etc.). The system will allow permanent monitoring of the quality of filtered water by utilizing MFC's output voltage dependence on inorganic contaminants and the response of the biosensor patented A/00764/26.10.2012, which detects the bacterial species *Escherichia coli, Salmonella spp., Listeria monocytogenes* and *Campylobacter jejuni.*

During this study we research: the influence of interconnecting the two stages of filtration, starting with the premise of isolating MFCs from the outside by the RO 127171 filter membrane to prevent further biological contamination with MFC's active microbes, determining different microbe cultures efficiencies in cleaning the oxidized contaminants, widening the detection array of the biosensor A/00764/26.10.2012, optimizing the automation and collecting system to increase lifespan but also to build an interface to publicly access the collected and processed data.

Each member state of European Union – including Romania, commits to achieve the standards for water quality for all water sources (including territorial waters) by 2016: biological quality, hydro-morphologic quality, physical and chemical qualities (temperature, oxygen levels, nutrients, limit of specific contaminants). Moreover, through Article 14, which acknowledges the Convention for Access to Information, Public Participation in Decision Making and Access to Environmental and Justice Matters, the interest of third party entities is encouraged.

Considering the topic – that of reducing the contaminants from the whole food chain (Kim BH, et al., 2003, Bretschger O., et al., 2010, Venkata M.S., et al., 2008), this study meets the HACCP (Hazard Analysis and Critical Point Control) framework, introduced by the National Consultative Committee for Microbiological Criteria of Foods (NACMCF, 1998) further extended by the Water Safety Plans of the World Health Organization, acknowledging the effect of contaminated water in all stages of food processing. Severe risks can be prevented by controlling water contaminants:

- Fecal pathogens: through water contamination with organic waste from farms, the pathogens life-cycle is completed. About 5.7 mil. Romanians contaminate the ground waters from the lack of a proper waste disposal network (acc. 2012 Romanian Census).
- although pathogens (with a few exceptions) are not multiplying in water, introducing them in food (drinking water for animals or used in technological processes) can produce epidemics.
- contaminants concentration is decreasing through dilution in time, but processing foods with contaminated water can create dangerous microorganisms build-ups.
- the economic effects of contaminated products – for example, the recent case of *E. coli* infected cucumbers has produced 400 mil. euro damage in 2011 (acc. European Commission reports) and another 150 mil. by

community support programs. Romania lost crops valued at 9 mil. euro in June 2011.

- water contamination is a major problem with high impact in the society. 1 bil. inhabitants lack access to safe water supplies, 14,000 people die every day from lack of drinking water, 84% of Romanian rural communities (almost 7.2 mil. people, acc. 2012 Romanian Census) lack access to drinking water supplies.
- Energy consumption to filter one cubic meter of water has increased from 634KWh in 2006 to 756KWh in 2007 (Bretschger O., et al., 2010), making the decontamination process for surface waters to be energy expensive, autonomous solutions being preferred in such situations.

Building a filtration device, simple to install and maintain, with small costs, to improve water quality through filtration and inactivation of biological and chemical agents becomes an opportunity from the perspective of the above mentioned: through direct impact on one third of Romania's population but also protecting the economy. Moreover, monitoring the water quality is a key component of the 310/2004 law, appending the 107/1996 Water Law, becoming a tool for the Environment and Forest Ministry and for National Environment Guards.

MATERIAL AND METHODS

Microbial Fuel Cells (MFC) are known from the beginning of the XX century, but only recently, through progress in the material science field, they found practical applications in producing electric energy using residual waters and at the same time decontaminating them. The working principle behind MFCs is using the carbohydrates stored energy by anaerobic anodic oxidation and cathodic reduction using electrons from the external circuit and protons from the internal ionic circuit. One of the reasons MFCs are researched heavily in the past 4 years is the discovery of exoelectrogen microorganisms, i.e. which have the ability to transfer electrons outside the cell. Classified in these are: *Shewanellaputrefaciens IR-1, Clostridium butyricum, Desulfuromonasacetoxidans, Geobactermetallireducens, Geobactersulfurreducens, Rhodoferaxferrireducens, Aeromonashydrophilia (A3), Pseudomonas aeruginosa, Desulfobulbuspropionicus, Geopsychrobacterelectrodiphilus, Geothrixfermentans, Shewanellaoneidensis DSP10, Escherichia coli, Rhodopseudomonaspalustris, Ochrobactrum anthropic YZ-1, Desulfovibriodesulfuricans, Acidiphilium sp.3.2Sup5, Klebsiella pneumonia L17, Thermincolasp. strain JR, Pichiaanomala.*

Most MFC utilize bacteria to process waste but combining it with the nanocompozite material RO 127171 for isolation and the A/00764/26.10.2012 for monitoring the activities of the microorganisms.

The patent no.RO127171, describes a method for the fabrication of a biodegradable multifunctionalized composite material that engraft in his structure four different structural components; each structural component of the composite contain different grafted chemical functionalities; the composite act as carrier substrate for deployment of different mechanisms and functions active in chemical reticulation processes.

The structural components and their associated functionalities are: a.) an oxidic fraction formulated in the form of a mixture of metal / non-metallic oxides and oxo-halogenated compounds of Fe, Al, Mg, Ca; b.) magnetite nanoparticles; c.) a fraction of metal oxides coated with thin layers of metal fluorides; d.) a polymeric matrix for the embedment of oxide nanoparticles which consist in a biodegradable polymeric material selected from a cellulosic constituents like paper and cellulose acetate.

Each structural component of composite material it is charged with a particular class and type of chemical functionalies which further are engaged in reticulation, degradation and / or encapsulation of specific types of biological contaminants like toxins, viruses, bacteria, or secondary metabolism degradation byproducts as follows: a.) the filtration material's oxidic constituent fraction promotes the reticulation, encapsulation, degradation and removal of biological contaminants (RRED-B process) due to its varied functionalization structure which consist in grafting of aminated-, hydroxylated-, thiolated-, carboxylated-, ester-, carbonylated- or mixt functionalized compounds containing previously mentioned functional groups; b.) aldehyde functionalized Fe_3O_4 nanoparticles promotes the contaminant's sedimentation by chemical and charge flocculation as well may promote their controlled separation in external magnetic / electric field; further, this functionalized substrate favour the reticulation and removal of biochemical contaminats carrying aminated- functionalities; d.) oxyfluorides have prophylactic functions by irreversible degradation of microorganism's structure and functionality beforehand encapsulated by composite material; d.) the embedment polymeric fraction (cellulose-type fractions) have a fibrilar structure that is structured at nano- and micrometric level: the functional structure of this component is able to reticulate contaminants with halogenated and hidroxylated functionality; by compositing processes it is able to host oxide fractions and Fe_3O_4 nanoparticles on its functionalized surfaces as well on its deep 3D framework composite structure the final outcome leading to the formation of neo-/micromembranary lattice that promote and help filtration process and its efficiency.

In agreement with the invention described in patent no.RO127171, the material and of its structural components are fabricated (chemically functionalized) in distinct stages of fabrication process as follow: stage 1 – the functionalization of oxidic mixture in the presence of BrCN / HCN; stage 2 – the functionalization / processing of cellulose-based fraction in the presence of a mixture containing acetone-dimethyl sulfoxide and epichlorohydrin-NaOH; stage 3 – distinct preparation of oxyfluoride fraction by using magnesium acetate and HF; stage 4 – the building of composite material by compositing

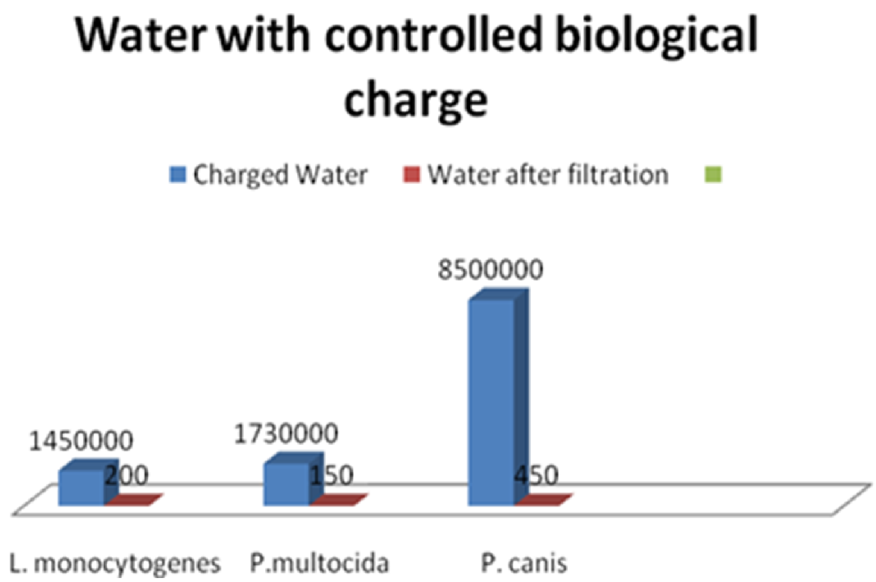

Figure 1. Water with controlled biological charge

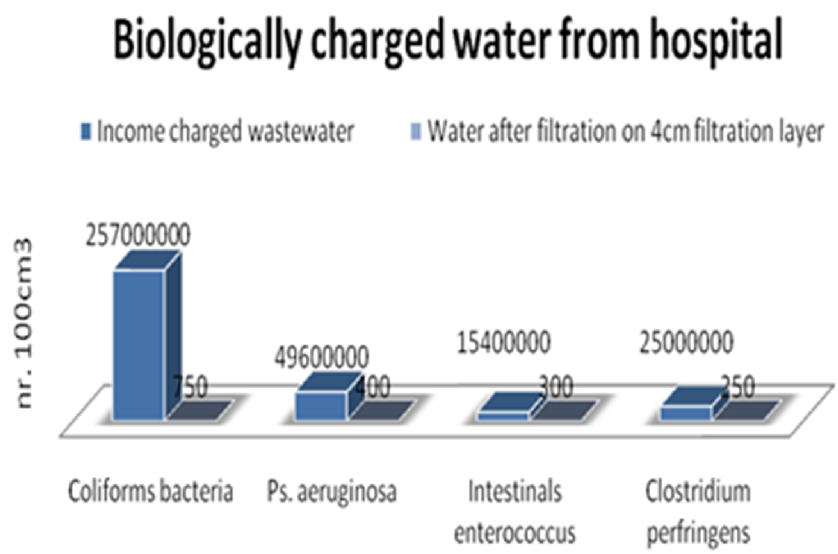

Figure 2. Biologically charged water from hospital

the intermediary fractions obtained in stages 1, 2 and 3 by their mixing at pH 12. The patent also describe a way for material's use that is formulated in the form of filters for biological depollution: in this case, the filters are made by composite's deposition and his compression between two layers of ordinare porous paper.

Biological contaminant's removal. The multifunctionality of material is brought in by its individual components whose functionality target the specifically chemical structures found on the surface of microorganisms and their intermediary degradation byproducts.

The internal composite structure of material was engineered to reticulate and encapsulate the biological contaminants. Mainly, the mechanisms for contaminant's removal involves the reticulation of functionalized material on the surface of biological contaminants like viruses, bacteria, through its high density functionalized surfaces; next, the process is followed by degradation the biological functions & functionality of microorganisms and, finally by the encapsulation of compounds that may result as secondary degradation byproducts. Before the saturation of the material, all reticulated compounds are fully neutralized and encapsulated into the deep 3D-framework structure of material.

In the Figure 1, 2 are presented few concludent testing reports obtained in the development stage of the material

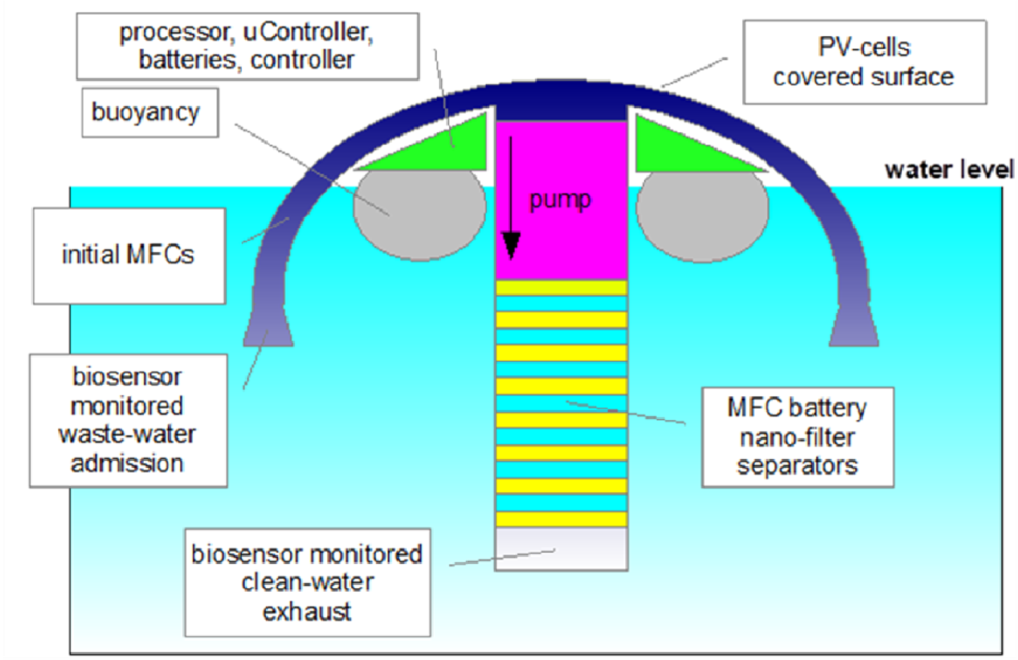

Figure 3. Device for monitoring and filtering surface contaminated waters

which point out the achieved level of removed contaminants and feasibility of proposed solution. The MFC will be self-cleaning, using ultrasound to break down cell walls and mince the residue which will be further processed by the anodic microorganisms, minimizing human intervention for keeping the device operational.

RESULTS AND DISCUSSIONS

The main goal of this study was to build a device for monitoring and filtering surface contaminated waters from mainly residential areas (wells, lakes, rivers) where the presence of biological and chemical contaminants affect the farm animals and the crops, which represent the basis of the food chain (Figure. 3).

To attain this goal a prototype device was constructed, that integrated to already obtained patents, one for a biosensor capable of detecting the microorganisms *Escherichia coli, Salmonella spp., Listeria monocytogenes*, *Campylobacter jejuni* (A/00764/26.10.2012) and one for a poly-functional material for filtration of biological pollutes (RO 127171) in the field of MFC – testing different configurations for MFC utilizing surface waters and experimental proving of the efficiency of their ability to reduce metallic compounds degrading at the same time organic waste.

The specific objects of this study are:

- (O1) Designing and building a battery of single-chambered mediator-free MFC, heterogenous, for detecting and monitoring bio-chemical contaminants in surface waters. The chemical parameters considered are the concentration of sulphates, chlorates, phosphates and nitrates, and for the biological part the number of individuals from species *Escherichia coli* (Venkata M.S., et al., 2008), *Staphylococcus aureus, Pseudomonas spp.* (Wrighton K.C., et al., 2011; Bretschger O., et al., 2010), *Proteus vulgaris* (Yuan Y., et al., 2011).
- (O2) Designing and building a bio-chemical filtration system for surface water pathogens, autonomous, adaptable, using poly-active nano-filters and heterogeneous bacteria single-chambered mediator-free MFCs. The contaminants considered are sulphates, chlorates, phosphates and nitrates, the species *Escherichia coli, Staphylococcus aureus, Pseudomonas spp., Proteus vulgaris*.
- (O3) Designing and building an embedded monitoring and controlling system, using biosensors, single-chambered, mediator-free MFC battery, poly-active nano-filters controlled with an ARM system-on-a-chip, self-powered using MFC energy combined with photovoltaic cells and rechargeable batteries for storage.

The technical problems addressed in this study are:

- Fast detection of different chemical contaminants concentration simultaneous using MFCs.
- Fast counting the microorganisms from several species simultaneous using MFCs.
- Creating a heterogeneous MFC battery. Even separated, the metabolites of one species can affect another's development.

- Optimizing filtering performance for different species used in single-chambered mediator-free MFCs.
- Building an autonomous device, self-powered, with self-cleaning filters to minimize human intervention and to convert it into a viable product.

The study completes the set of equipment`s and technologies in the field of cleaning surface waters through the following attributes:

Taking advantage of the patent RO 127171 for the nano-compozite material used in water filtration systems for isolating microorganisms used in MFCs, the decontamination system sets as innovation the utilization of a battery of heterogeneous MFCs, minimizing bacterial colonies interaction and widening the array of processes contaminants.

The voltage produced in MFCs can be used to detect in real-time the biochemical oxygen demand (BOD). The innovation consists in using the heterogeneous MFCs, the different species metabolism to qualitative and quantitative simultaneous determination for a wide range of contaminants. The lifetime for such a device is quite large - over 5 years, (Kim B.H., et al., 2003),making it economical important. The monitoring component of the system will be backed by the biosensor patented A/00764/26.10.2012.

The system is autonomous. This will use MFC energy supplemented by PV-cells and backup rechargeable batteries. For controlling the pump, the individual cells of the MFC battery an ARM based platform will be used to gather data and take decisions based on observations. GSM and Wi-Fi connectivity is expected by using popular data interfaces (USB, serial).

Using in conjunction the three elements presented above emphasis the innovative character of the study, combining elements proven successful (the nano-filters, the biosensor, ARM platform for data acquisition) with new elements, with proven conceptual models, integrated in a series of existing products, though never used in this way (the heterogeneous MFC battery, used both for energy production, decontamination and water quality monitoring).

Currently the number of products intended for filtration of surface water is relatively large: mechanical filters (with different filtration media that do not allow the passage of contaminants with diameters higher than a fixed reference, usually larger than 200 nm for membrane filters), chemo-mechanical filters (that introduce an agent to flocculate the contaminants and filter them mechanically), chemical filtration (by treating the water with chemicals to inactivate the contaminants), biological filtration (inserting benign microorganisms that metabolizes contaminants), dissolved ion filter (with ultrafiltration membranes, ion exchangers, electrical removal of ions), etc.

This products presents a series of limits determined by the reduced bioavailability, the presence of side effects like chemical or biological contamination given the complex protocols needed to be implemented, the high specificity of this filters, high energy consumption for pumping and treatment (estimated to 756KWh/mc drinking water in 2007(Velasquez-Orta, et al., 2011) high maintenance costs.

Given the incidence of *E. coli* infections (microorganisms from the digestive tract of ruminants, released in the environment through fecal matter and quickly contaminates the surface waters, affecting both animals and crops), *S. aureus* (organisms present in 25% of the nostrils of people, highly resistant, that can generate damaging food poisoning, with antibiotic immune strains that grow in incidence: MRSA and CA-MRSSA), *Pseudomonas spp.* (especially *P. aeruginosa* which is an opportunistic pathogen with high clinical importance; present in water, is one of the widest studied bacteria; recently, antibiotic resistant colonies were discovered (Van Eldere J., 2003), *P. vulgaris* (present in the intestines of a large set of animals but also in humans, is a contaminant common to surface waters and is the main cause for urinary tract infections, being the cause of 10-15% of kidney stones (Keefe W.E., 1976), a complex strategy for decontamination and monitoring is necessary for prevention and removal. At the same time, the 4 species of organisms are exo-electrogenic (Venkata M.S., et al., 2008; Wrighton K.C., et al., 2011; Bretschger O., et al., 2010), making them perfect for usage in single-chambered mediator-free MFCs for removal of sulphates, chlorates, phosphates and nitrates with redox bio-catalytically induced reactions, generating electrical currents that can be used for powering control electronics and for monitoring the contaminants.

Local availability of the microorganisms (frequently encountered in surface waters) demand creation of a system that can trap them in the filtering column, using for this purpose the material RO 127171. Fast monitoring will be also implemented by integrating the A/00764/2012 biosensor, getting a full system for monitoring and filtering surface waters.

This study will lead to getting a non-toxic, highly efficient, biochemical filtering device by:

- increasing the bioavailability;
- speculating biochemical and electrical properties of the involved microorganisms;
- synergistic actions of the bio-complex and those of the nano-material, amplified by auto-assembly (of biofilms) and electronic control.

CONCLUSIONS

This study will directly contribute to improve the quality of life in Vatra Dornei through the following aspects:

- Developing and standardize a biotechnology for innovating decontamination and monitoring, with the opportunity to widen the applications for other species of microorganisms and/or contaminants.
- Getting a device for decontamination and monitoring surface waters with direct consequences in

improving the health and diminishing the treatment costs by implementing prevention.

- The possibility of industrial applications, building the premises for developing new economic profit-oriented activities.
- Detection and prevention of bio-hazards with major socio-economic impact (ex. The problem with *E. coli* infected cucumbers).
- Value added apart for the product, the elements used being organic, non-polluting, locally available, biodegradable, autonomous (decreasing energy requirements), with low-cost maintenance by medium-qualified technicians (generating jobs).

The social estimated impact resulting from the implementation of the project:

- Creating new jobs for medium-qualified personnel involved in assembly and maintenance of the equipment`s, but also jobs with higher occupational standards: developing scientific and managerial competences at high level;
- Direct impact on beneficiaries, by building low cost devices, simple to use, autonomous, that filter the surface waters most likely used in farming and food preparation.
- Increasing quality and quantity of information`s regarding MFCs' practical applications.
- Positive impact on the environment, by monitoring contaminants and centrally reporting the data, but also by using biocompatible and biodegradable devices and technologies as active factors in decontamination and monitoring. Technical solutions will be correlated with environment local, European and world standards for increasing the quality of water. Moreover, the results of the project can be directly used at national level to meet the 2000/60/EC directive goals, that by 2015, all water sources have to comply with standards for water quality.

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