Municipal Wastewater Treatment, Ecological Component of Strategic Synergy in the Black Sea Basin

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The Black Sea is one of the world's most polluted seas. Chemicals such as oil, fertilizers, insecticides and herbicides which do not decompose in the ground, enter the Black Sea, which becomes a huge repository for these collections mixed fertilizers and poisons. Domestic wastewater significantly contributes to pollution with organic matter and nutrients, and may be responsible for the spreading of diseases. A major component of the synergistic strategies for the environmental protection of the Black Sea consists the proper wastewater treatment. It is necessary to limit the amounts of nutrients such as ammonia, which may be discharged in treated effluents, to prevent excessive growths of algae and aquatic plants that can cause serious harm or even destroy the aesthetic value of water. In the frame of a case study, on the base of Bardenpho process, the simulation of remediation the increasing of ammonia concentration in municipal wastewater effluents was done using the SuperPro Designer v8.5 simulator. The reducing of ammonia concentrations in effluent was realized by modifications of several operating process parameters and the ammonia concentrations in effluent were decreased below the maximum legal admitted concentration. Also it was investigated the effect of the recirculated flow rate over the effluent ammonia concentration and over the total operating cost, which is a multiobjective optimization problem.

Keywords: synergistic strategies, municipal wastewater treatment, ammonia effluent concentration, Bardenpho process, computer simulation

Synergy is the combination of two or more things that creates an effect which is greater than the sum of each separately [1]. In the natural world, synergistic phenomena are ubiquitous, ranging from physics (for example, the different combinations of quarks that produce protons and neutrons) to chemistry (a popular example is water, a compound of hydrogen and oxygen), to the cooperative interactions among the genes in genomes, the division of labor in bacterial colonies, the synergies of scale in multi-cellular organisms, as well as the many different kinds of synergies produced by socially-organized groups. Even the tools and technologies that are widespread in the natural world represent important sources of synergistic effects which have been the drivers of cooperative relationships of all kinds and at all levels in living systems. Environmental systems may react in a non-linear way to perturbations, such as climate change, so that the outcome may be greater than the sum of the individual component alterations. Synergistic responses are a complicating factor in environmental modeling [2].

Black Sea is plased between 40°55' and 46°32' north and 27°27' and 41°42' east. Black Sea is part of the typical continental seas, communicating with Marmara Sea through the Bosporus and the Aegean through the Dardanelles. Black Sea is a graphical component of European significance which defines the geographical position of our country. Romania is a Pontic country through its 244 km coastline held at arm's Musura Chilia secondary delta in the north to Vama Veche in the south. The sea surface is 411540 square kilometers, being the third largest in Europe after the North Sea and the Mediterranean Sea. The maximum depth is 2246 m in the south-central region, and the average depth is 1200 m. Water depth around the Romanian banks is lower, as a result configuration shore, and submarine relief. Black Sea has a regular shape, shores are generally less articulated and without the islands. The basin next to the Romanian shore is a large continental platform with depths not exceeding 200 m.

Gheorghe Bratianu [3] emphasized the implications which Black Sea has had on neighboring space, and, especially, on the Romanian regions: The pontica problem is more complex. It's really a almost closed sea, which does not communicate with the Mediterranean only by narrow output straits; however due to the large rivers flowing into it from the depths steppes or massive of Central Europe, due to the network of continental roads arriving in its ports, she deserves, as much as other more open higher currents offshore, the name of *turntable* the great traffic and the international exchanges. This feature of the transition and the crossroads between Europe and Asia is printed to the peoples and states established its coast. Due to this maritime factor the Romanian history is different that the history of the countries remaining far from major trade routes and sheltered from war. These countries are much happier in periods of crisis, because do not attract a too supported attention to the diplomats and strategists. We are dealing here without doubt the inevitable reverse of the medal: historical interest that awakens a geographic region is a privilege to be paid dearly. Anyway, Romanian history can not be understood without taking into account the influences of the intersecting roads in the territory where it evolved, made him a true crossroads of civilization and trade, but also, unfortunately, invasions and wars. Geopolitically, the Black Sea is, by force things, at the forefront of interest and research [3].

Black Sea pollution

The Black Sea is one of the world's most polluted seas [4]. In the Black Sea drains the waters of 17 countries that carry out substantial economic activities. Danube is the main transmitter of pollutants. Chemicals seeping through the ground water and rivers are so worn there to the Danube

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and the Black Sea. Chemicals such as oil, fertilizers, insecticides and herbicides which do not decompose in the ground enter the Black Sea, which becomes a huge repository for these collections mixed fertilizers and poisons. Outside pollutants brought by large rivers, large quantities are discharged into coastal areas and coastal towns by transport activities. These have a strong impact on the near shore flora and fauna and on human activities, especially fishing and tourism. In the Black Sea basin now living over 165 million people, most of them unaware that actively participates in pollution one of the most degraded seas on the planet. Crude oil and other petrochemicals are the main polluters of the Black Sea, with the sewage, household garbage and air pollution adds significantly. Black Sea vulnerability is due to its isolation and due to the large scale of land-based pollution sources. On the Black Sea basin the intake of sediments carried by the river decreased, due to the interruption in the reservoirs whose number and importance grew throughout the Danube river basin, by dams and reservoirs for the production of electricity, but also by the use of irrigation water. By reducing the amount of water, the Danube contributes to the retention of the continental sediment pollutants. It takes place a pronounced erosion of the beach and shore, simultaneously with increased flowering due to the intake of seawater and direct discharges Danube biogenic substances. Most of the Black Sea continental shelf and especially to the northwest is highly eutrophic. Annual, the Danube is bringing almost 60,000 tones phosphorus and around 340,000 tones inorganic nitrogen. In the past 25 years we have seen a dramatic increase in the amount of nutrients, especially due to the widespread use detergents with phosphates and due to the expansion of intensive agriculture. In moderate amounts, nutrients used as fertilizers (nitrogen and phosphorus) are beneficial, they are indispensable for the functioning of ecosystems. In a first phase, they have the effect of increasing the overall amount of food (more algae, more sprat, more sardines, etc.). But excessive amounts of nutrients can have devastating effects. As the increase of their amount, as an adaptation to the changed ratio of nutrients, the composition of phytoplankton is altered. These sudden changes in the quantity of nutrients are sometimes manifested by *blooms* of some algae, which are toxic or less nutritional for animals. These disturbances, as the abundance of food, allowing the proliferation of jellyfish and Comb jelly, which bypasses the food chain because they do not have natural predators in the Black Sea. The massive blooms of algae since 1975, together with associated phenomena (consistency mucilaginous water, the smell of seaweed and rotten fish, tons of mussels and dead fish thrown on the beach subject to putrefaction, insects and rodents carrying diseases around them) have it had an important role. There are not neglected the negative psychological effects on tourists and local people (wonder about changing water color to crimson, the feeling of fear that arises, especially when phenomena are accompanied by massive fish mortality), as happened in 1992, 1998 and 1999. Eutrophication and other ecosystem degradation have reduced biodiversity and seriously disturbed the equilibrium of ecosystems in the Black Sea. In the last 25-30 years, the Black Sea was transformed from a diverse ecosystem, with a great variety of numerous species, in an eutrophic culture of algae, with environmental unsuitable conditions for the most organisms from the upper part of the trophic pyramid. Even deeper areas are seriously modified, with no 50% of the species that populate in 1967-1970, and the biomasses are ten times lower than those of a few decades ago. Zostera and Cystoseira fields disappeared and Phylophora algae biomass is estimated at about one tenth the past. With them they have gone many other species that were in trophic connection. The biomass of other species, important to the food chain of the Black Sea, was also greatly reduced: shell Corbula number was reduced to 240 times, and the biomass of clam Mytilus was reduced by 70%.

The main source of pollution in areas near towns on the coast is the untreated or insufficient treatment of wastewater. Domestic wastewater significantly contributes to pollution with organic matter and nutrients, and may be responsible for the spreading of diseases. For most coastal cities, sewage discharged into the sea does not have sufficient quality due to the under sizing of treatment plants, their low efficiency, and due to the infringement of the rules on the discharge of industrial wastewater into municipal sewers. Due to the conflicting reports and the lack of transparent information sources, it is difficult to estimate the Black Sea pollution. The environmental problems in the Black Sea caused large economic losses. In the fisheries sector, the losses for entire basin are estimated at 240 million dollars annually, and for tourism between 340-400 million dollars annually. Costs to decrease pollution, such as health or unemployment, are also enormous. If will be consider the number of lost workdays, the healthcare cost, the cost for reintroduction of extinct species, the damage caused by erosion, and the cost to identify of alternative water supply, the annual bill could exceed at the scale of the entire basin one billion dollars annually. To this must be added indirect effects related to the privatization of state enterprises and development of private enterprises. Pollution from inadequately treated wastewater has increased the number of gastrointestinal diseases. If sanitary regulations were met, it would cause huge losses for tourism, and if not met, there is always a risk of illness. The presence of a large number of people living or vacationing on the Black Sea seriously affect the coastal environment, overloading drinking water and biological resources, and so affected. High consumption of water due to inefficiency of many facilities, is a potential risk for the future.

Synergistic strategies against Black Sea pollution

The study and protection of seas and oceans are managed by the International Hydrological Organization (IHO), founded in 1921 on the initiative of Prince Albert I of Monaco. This organization brings together more than 80 countries that have a maritime border, and its headquarters are in Principality of Monaco [5].

In the Black Sea basin, Romania, Bulgaria, Turkey, Georgia, Russia and Ukraine signed in Bucharest the Declaration for the protection of the Black Sea against pollution. But the major problem is lack of the integrated management of coastal zone (with the integration of all sectors in coastal zone involved in decision-making). Although the Black Sea countries are trying from long time to stop the degradation, they need specialized international assistance. The political changes in the region over the past 25 years have created the opportunity for national and international actions to save the Black Sea. The first step was the launching of the *Environmental Management and Protection of the Black Sea Program,* ran from 1992 - 1996, a program funded by Global Environment Found, a trust formed by World Bank, United Nations Development Programme, and United Nations Environment Program. This international program aims to be a catalyst for rehabilitation of the environment and its sustainable use and was completed, among other things, with the signing of the Strategic Action Plan for the Black Sea. The development program about implementation of The Strategic Action Plan for the Black Sea is mainly focused on developing and implementing of the National Strategic Action Plans at Black Sea.

A major component of the synergistic strategies for the environmental protection of the Black Sea consists, as was mentioned, the proper wastewater treatment. The wastewater discharges is one of the key factors of European policy, considering that they come in mostly from human activities, and they may lead to water pollution, respectively to negative effects on aquatic ecosystems and on human health. Based on the principles of water sustainable development and management, all the water users which discharge wastewater into natural receivers and are owning a regulatory act in terms of water management are potential sources of pollution, and are subject to an annual monitoring control [6].

The wastewater monitoring follows:

-the compliance of the discharge conditions established by the water management authorization;

-the knowledge of water resources (emissions-imissions), of their protection against depletion and degradation, and enhancement of their sustainable use;

-elaboration of the specific reports on emissions of pollutants into natural receivers.

As the impact of pollution sources on natural receptors depends on the effluent flow rate and pollutants load, the control monitoring of the wastewater include: measuring of wastewater volumes, determining quality indicators and determining the operation of the wastewater treatment plants. The processing of wastewater quality data consists in the appreciation of the average pollutants load. Thus, for the human agglomerations, the main groups of pollutants with significant contribution to the degree of pollution of the natural receptor are: organic substances, nutrients, materials in suspension, extractable and detergents. The reducing of the amounts of these pollutants is the result of the measures to increase the efficiency in the operation of the wastewater treatment plants and also of the construction, expansion and modernization of urban waste water treatment plants.

The aforementioned ideas will be materialized through the following case study.

Case study

Simulation and control of wastewater treatment plant discharged into the Black Sea.

The need for removal of ammonia from treated municipal wastewater effluents is a very important task. Ammonia is a nutrient and the growth of aquatic plants can thrive in its presence. It is necessary to limit the amounts of nutrients such as ammonia which may be discharged in treated effluents to prevent excessive growths of algae and aquatic plants that can cause serious harm or even destroy the aesthetic value of water.

The Bardenpho process is one of the most applied techniques for nitrogen removal. The Bardenpho process is a single-sludge system comprised of four alternating anoxic and aerobic zones in series (Figure 1). The first and third zones are anoxic while the second and fourth zones are aerobic. Mixed liquor is recycled from the first aerobic zone to the first anoxic zone at a rate of four to six times the influent flow rate. Return activated sludge is also recycled from the clarifier back to the first anoxic zone. This process is designed to achieve more total nitrogen removal than is possible with two-sludge or three-sludge systems.

The Pro-Designer flowsheet [7] for simulation of Bardenpho process (fig. 2) shows the two anoxic and two aerobic stages as separate process units. In reality, all four stages are accommodated by the four initial tanks. A single icon on the flowsheet may represent multiple identical units operating in parallel.

For a reference case the input flowrate is 1901.225 m^3/h and the influent and effluent concentrations are indicated in table 1.

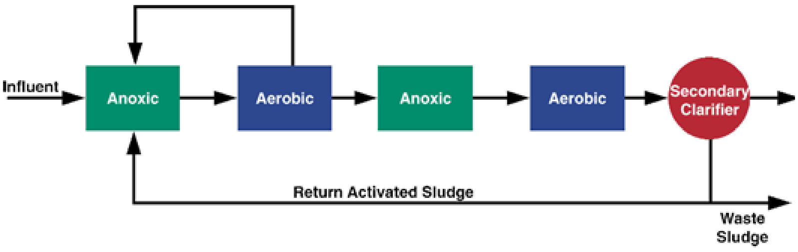

Fig.1. The Bardenpho process

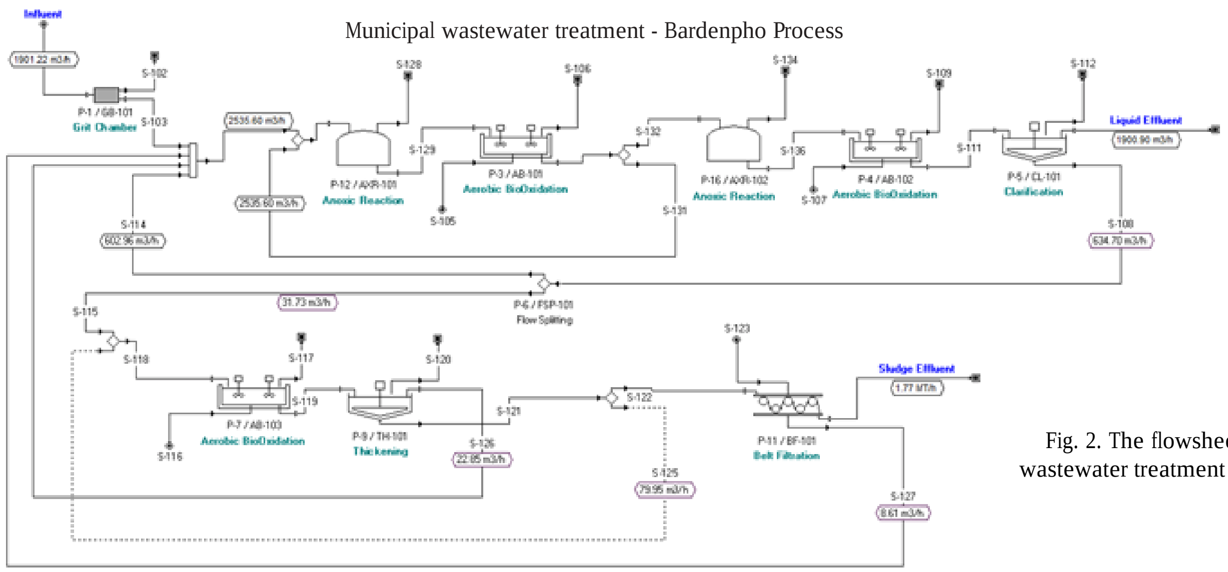

Fig. 2. The flowsheet of a wastewater treatment plant [7]

Table 1
INFLUENT AND EFFLUENT REFERENCE CONCENTRATIONS

Component	Reference influent concentration (mg/L)	Reference effluent concentration (mg/L)	Explanation
DomWaste	105.1953	0.6045	substrate - organic, soluble, biodegradable material
X-vss-h	52.5977	34.8422	active volatile solids in suspension (heterotrophic biomass)
X-vss-i	51.0197	15.7968	inert volatile solids in suspension
X-vss-n	3.1559	0.9698	vss for nitrifiers (autotrophic biomass)
FSS	60.4873	14.5330	fixed suspended solids (non-biodegradable)
TDS	305.0665	304.9001	total dissolved solids (non-biodegradable)
NO_3	2.6299	0.6690	nitrite/nitrate
Ammonia	13.1494	1.8671	dissolved NH_3/NH_4 (not NH_3-N)
Carbon Dioxide	51.0197	0.1396	dissolved CO_2 (in the form of HCO_3 or H_2CO_3)

Table 2
REMEDIATION OF INCREASING OF AMMONIA CONCENTRATION

Component	Influent concentration for the case of ammonia increasing (mg/L)	Wrong regime effluent concentration (mg/L)	Remediated regime effluent concentration (mg/L)
DomWaste	105.6669	0.4078	0.7606
X-vss-h	52.8335	36.6556	38.1164
X-vss-i	51.2485	15.8673	15.9064
X-vss-n	3.1700	1.0222	0.9621
FSS	60.7585	14.5979	14.5974
TDS	306.4341	306.2797	306.2582
NO_3	2.6417	1.0755	14.0313
Ammonia	21.1334	8.9518	0.6704
Carbon Dioxide	51.2485	0.1123	0.2436

The detailed stoichiometry equations and kinetic constants of substrate (DomWaste) degradation, nitrification, biomass decay, and de-nitrification can be found in the literature [8, 9].

Two important applications are studied: a) simulation and remediation of an increasing of ammonia concentration**;** b) effect of the recirculated flow rate over the effluent ammonia concentration and over the total operating cost.

a)Simulation and remediation of increasing of ammonia concentration.

It is assumed an increasing of ammonia influent concentration resulting in an over the legal limit ammonia effluent concentration (8.9518 in table 2). The maximum admitted value of ammonia effluent concentration is 2 mg/L [10].

In order to remediate this situation the following modifications of the operating process parameters were made:

-the residence time of the first anoxic reaction zone was decreased from 0.421 h to 0.025 h (a decreasing with 94%);

-the residence time of the second anoxic reaction zone was decreased from 0.631 h to 0.037 h (a decreasing with 94%);

-the residence time of the first aerobic bio-oxidation zone was increased from 0.842 h to 0.887 h (an increasing with 5%);

-the residence time of the second aerobic bio-oxidation zone was increased from 0.210 h to 0.222 h (an increasing with 5%);

-the flowrates of diffused air for the first aerobic bio-oxidation zone was 5 times increased from 0.6 m^3/h to 3 m^3/h;

-the flowrates of diffused air for the second aerobic bio-oxidation zone was 20 times increased from 0.6 m^3/h to 12 m^3/h.

The residence times were modified in agreement with the restrictions over the working volumes limits. The reasons of the above modifications of the operating process parameters were to reduce the denitrification in the anoxic reaction zones, and to increase the nitrification in the aerobic bio-oxidation zones.

As result of these modifications of the operating process parameters the effluent ammonia concentration was reduced at 0.6704 mg/L (table 2), therefore under the maximum admitted value of 2 mg/L. Also, it can be observed that nitrite/nitrate effluent concentration remain in the accepted limit, respectively 14.0313, the maximum admitted value of nitrite/nitrate effluent concentration being 25 mg/L [10]. Therefore the modifications of the operating process parameters for decreasing of ammonia effluent concentration did not increase nitrite/nitrate effluent concentration too much, over the legal limit.

b) Effect of the recirculated flow rate over the effluent ammonia concentration and over the total operating cost.

Increasing of the recirculated flow rate gives a decreasing of ammonia concentration in the effluent, but will increase the total operating cost, due to increasing of pumping energy.

The value of recirculation rate at flow splitting FPS101 is for reference case (table 1) 0.95 to top stream S114. In the range 0.90- 0.99, by regression of the values of the effluent ammonia concentration x_{amm} (expressed in mg/L) in function of the recircularing rate r, it was obtained the equation (1):

$$x_{amm} = -0.01817\,r^3 + 0.10902\,r^2 - 0.29786\,r + 1.25166 \qquad (1)$$

The average relative error of this regression is 0.34 %, and the maximum relative error is 0.77%.

In the same range 0.90 – 0.99, by regression of the values of the relative power consumption for recirculation $P_{rel} = P/P_{95}$ (where P_{95} is the power for recirculation at recirculating rate r of 0.95) in function of the recirculating rate r, it was obtained the equation (2):

$$P_{rel} = r \,/\, (16.03519 - 19.11056\,r + 3.40788\,r^2) \qquad (2)$$

The average relative error of this regression is 0.40 %, and the maximum relative error is 0.67%.

The data for the regression equations (1) and (2) were obtained with SuperPro Designer simulations and the regression equations by the use of the software DataFit 8.1.

Establishment of the best value of recirculating rate r which minimize in the same time the minimum values of the effluent ammonia concentration given by rel. (1) and of the power consumption given by rel (2), with restriction $0.9 \le r \le 0.99$, is a multiobjective optimization problem (MOO).

Unlike single objective optimization, in a MOO, there will be in general multiple points which are optimal in the sense that an improvement in one objective can only be achieved with a worsening of one or more of the other ones. These optimal solutions are known as Pareto-optimal. The set of all Pareto-optimal solutions is usually referred as the Pareto front. In the absence of any further information about the problem, no solution can be said to be better than another and, ideally, the entire Pareto-optimal set should be found [11]. A number of MOO programs are readily available for academic and industrial use. In the present work is used one of these methods, respectively Matlab *gamultiobj* function, based on a genetic algorithm (GA). The Matlab GA *gamultiobj* , uses a controlled elitist genetic algorithm. GAs are stochastic search techniques that evolve a population of initial solutions. An elitist GA always favors individuals with better fitness value (rank). A controlled elitist GA also favors individuals that can help increase the diversity of the population even if they have a lower fitness value [12,13]. It is important to maintain the diversity of population for convergence to an optimal Pareto front. Diversity is maintained by controlling the elite members of the population as the algorithm progresses. Two options, ParetoFraction and DistanceFcn, control the elitism. ParetoFraction limits the number of individuals on the Pareto front (elite members). The distance function, selected by DistanceFcn, helps to maintain diversity on a front by favoring individuals that are relatively far away on the front. By adequate selection of the algorithm parameters the global optimum, or close near optimum solution may be obtained. To use the *gamultiobj* function, it must be provided at least two input arguments, a fitness function, and the number of variables in the problem. The first two output arguments returned by *gamultiobj* are **x**, the points on Pareto front, and Fval, the objective function values at the values **x**. A third output argument, exitFlag, tells you the reason why *gamultiobj* stopped. A fourth argument, Output, contains information about the performance of the solver; *gamultiobj* can also return a fifth argument, Population, that contains the population when *gamultiobj* terminated and a sixth argument, Score, which contains the function values of all objectives for Population when *gamultiobj* terminated. By default, the *gamultiobj* solver only passes in one point at a time to the fitness function. However, if the fitness function is vectorized to accept a set of points and returns a set of function values it can speed up the solution. The *gamultiobj* solver can accept one or more plot functions through the options argument. This feature is useful for visualizing the performance of the solver at run time. Plot functions can be selected using function *gaoptimset*. A plot function is *gaplotpareto*, which plots the Pareto front (limited to any three objectives) at every generation. The plot function *gaplotscorediversity* gives the score diversity for each objective. The options structure is passed as the last argument to the solver.

For the GA gamultiobj here were used the next options: population size: 60; selection function: tournament with the default value 2 of tournament size; reproduction using scattered crossover function, with the default value 0.8 of crossover fraction; adaptive feasible mutation; migration in forward direction with the default value 0.2 of migration fraction, at the default value 20 of the migration interval. The settings of MOOP were: @distancecrowding for distance measure function, and 0.7 for Pareto front population fraction. The stopping criteria were: 1200 generations, and 10^{-4} (the default value) for tolerance.

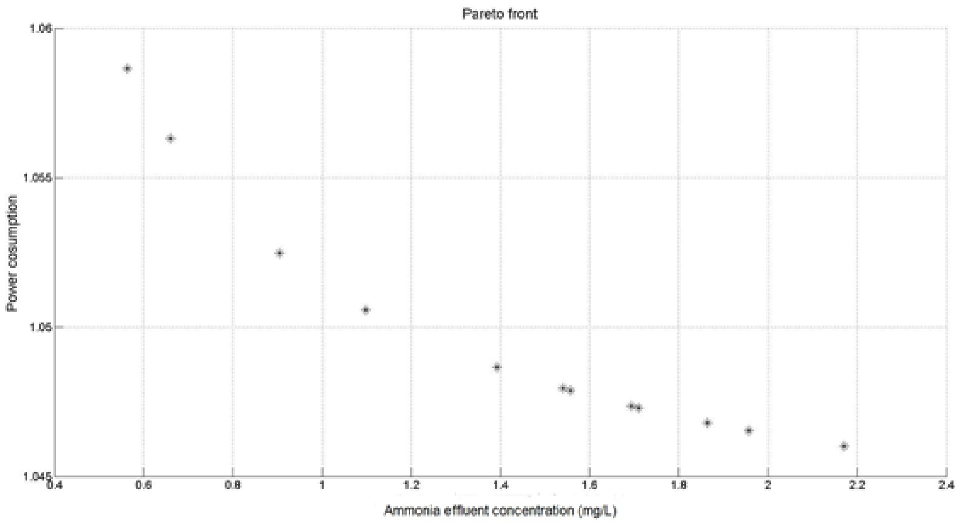

Fig. 3. Pareto front

The Pareto-optimal front is presented in figure 3. From these all optimal solutions can be selected the solution corresponding to the best compromise of the two objectives.

An other ecological component of strategic synergy together with the municipal wastewater treatment, can be the biological treatment of groundwater intended to human consumption [14,15].

Conclusions

A major component of the synergistic strategies for the environmental protection of the Black Sea consists the proper wastewater treatment. It is of paramount importance to limit the nutrient effluent concentration, such ammonia, to prevent excessive growths of algae and aquatic plants that can cause serious harm or even destroy the aesthetic value of water. In this paper was presented the decreasing of effluent ammonia from 8.9518 mg/L to 0.6704 mg/L (below the maximum admitted concentration of 2 mg/L) by modifications of several operating process parameters, using mathematical modeling and computer simulation. In the frame of a multiobjective optimization problem it was investigated the effect of the recirculated flow rate over the effluent ammonia concentration and over the total operating cost.

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