Romanian Journal of Petroleum & Gas Technology
VOL. IV (LXXV) • No. 1/2023

INNOVATIVE TREATMENT SOLUTIONS FOR OIL POLLUTED WATER

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DOI: 10.51865/JPGT.2023.01.20

ABSTRACT

Oil polluted water is not rare on the Earth and treating it in energy efficiency way to be properly returned to the environment is of great interest. This work makes an analysis of several technologies and selects some of them to be included into a complex treatment system starting from polluted water found in various places on Earth to the level of being released in nature, or event to use the treated water in human activities. Several stages of treatment are set: solid separation, oil separation, remained water treatment, filtration and evacuation. Separation of solids is made with less used and more energy efficiency technology. Also, oil from water separation is made with a new and very efficient technology, permitting future recovery of the separated oil for energy or semi-green hydrogen production. After releasing solids and removable oil, the polluted water is treated in more efficient way with natural components and with no polluting output based on ozone, oxygen and nitrogen gases in nano-bubbles form. All gases are extracted from natural air and converted in strong reactors through equipment presented in the work. The nanobubbles treated water releases the reaction by-products as oxides of metals to be filtered and oxygen, hydrogen, nitrogen, CO_2 gases to be released into the atmosphere before being clean to be released to the emissary.

Keywords: ozone, nano-bubbles, oil polluted water treatment, detergent, pesticide polluted water treatment

INTRODUCTION

The treatment of surface water pollution (hydrocarbons that make up films) can be achieved by:

- processes of dispersion of hydrocarbons throughout the mass treated with surfactants;
- direct or assisted pumping procedures that are applied in accidental pollution have the disadvantage that they are non-selective;
- adsorption-based processes; may be non-recoverable and recuperative.

Traditional techniques for separating water from hydrocarbons consist of hydrocarbon separators, centrifuges, flotation technologies, sedimentation technologies and are

suitable for non-emulsified, easily differentiable mixtures, but are not suitable for emulsions.

The separation of emulsions – stable water-hydrocarbon mixtures – is difficult and more complex for emulsions with a particle below 20 mm; where the means of intervention are much lower.

Emulsion separation technologies focused on two directions:

- water retention and release of hydrocarbons,
- retention of hydrocarbons and release of water.

The recuperative procedures use drums, discs, recovery strips, skimmers, membranes or spheres of nano-clays. Example: SurfCleaner, Figure 1 [www.surfcleaner.com] [1]

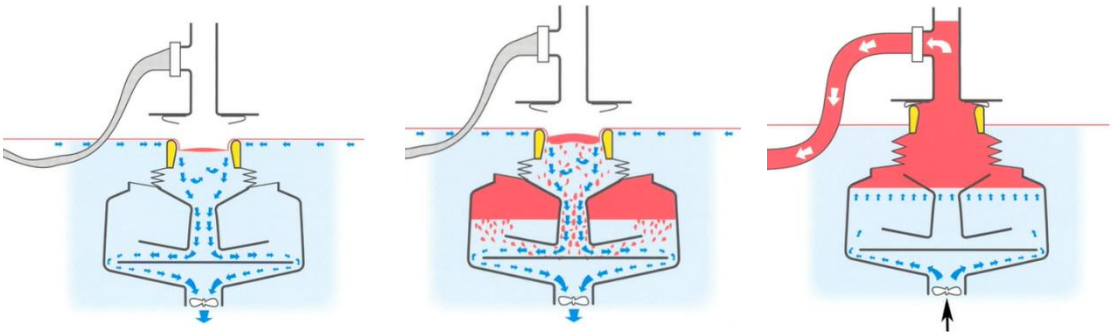

***Figure 1**. SurfCleaner [1]*

This installation is distinguished by the innovations brought: without using water pumps for absorption or operation, only natural phenomena, the inlet of polluted liquid is made in the device by buoyancy at the level of the superficial film, the liquid progresses gravitationally towards the lower area of the device. Inside the device, the water with hydrocarbon mass moves in the horizontal plane, pushed by the new mass of liquid entered into the device, where, through the plate separator, water is separated from the hydrocarbon on the basis of the different coalescence of the liquids. The hydrocarbon, being lighter, is collected in the upper area of the tanks, while the released by the hydrocarbon water is heavier and exits the device through the lower central part. When fully charged with hydrocarbon, the water acts as a piston that presses on the hydrocarbon mass which is discharged onto the upper tube. Collected and discharged into a container, the hydrocarbon separated from the water can be recycled. The device invented, produced and distributed by a Swedish company has a special demand on the market, recovering both hydrocarbons and clean water.

ADVANCED METHODS OF WATER DEPOLLUTION

1. Ozone use in polluted water treatment

- *Installed oxygen production by zeolite separation*

One installation separating oxygen from the air is the one in Figure 2, oxygen purity 93-95%.

***Figure 2**. Separation of oxygen and nitrogen from air plant [2]*

After drying, the air is introduced by the compressor into one of the separation recipients, container 1, until the working zeolite is charged with the gases it retains – nitrogen N_2, CO_2, the other gases – leaving the O_2 oxygen at the outlet, the air access to the 2nd container being closed. At the expiry of the working time for container 1, the solenoid valves close the air access to container 1, open the access of air to container 2, open the access of oxygen from the output of the container 1 for purging the retained gases and open the output of the container 2 for the release of the oxygen separated from air. The process continues for the second container till its working time expires. Then step 1 starts.

The oxygen separated from the 2 containers is stored in the intermediate equalization tank, and the other gases – nitrogen N_2, carbon dioxide CO_2, – if they are not needed, are purged in the surrounding atmosphere.

Zeolite that retains nitrogen, carbon dioxide and other gases except oxygen is called the "molecular sieve of lithium", being an alumosilicate contaminated with lithium, with type X structure.

The same equipment produces N_2 nitrogen with 98-99% purity, by collecting this flow, in the specific cylinder and delivery in circuit or specific cylinders. [3]

- *Installed ozone production*

Naturally, ozone is produced from oxygen in air with the help of energy from light, ultraviolet zone, 100 to 240 nm. It is also the UV radiation in the 200-315 nm range that destroys the trivalent bond of O_3 ozone, returning it in a biatomic connection to O_2. Also naturally, ozone also occurs at atmospheric discharge of lightning, which ionizes biatomic

oxygen and forms the ozone trimolecular. In the upper layers of the atmosphere ozone is maintained for a long time due to very low temperatures.

Ozone is produced industrially in several technologies from air or oxygen gas: by high voltage corona discharging, by UV radiation in the range of 100-240 nm, produced by mercury vapor fields and by electrolysis.

The block scheme of the oxygen ozone production plant by corona type electric discharge, is presented in figure 3, where:

- the ground electrode is connected to the assembly of the installation, made of stainless steel pipe, is located on the outside and is cooled by water;
- the inside electrode is applied the high voltage energy, it is electrically insulated with a glass tube from the ground electrode.

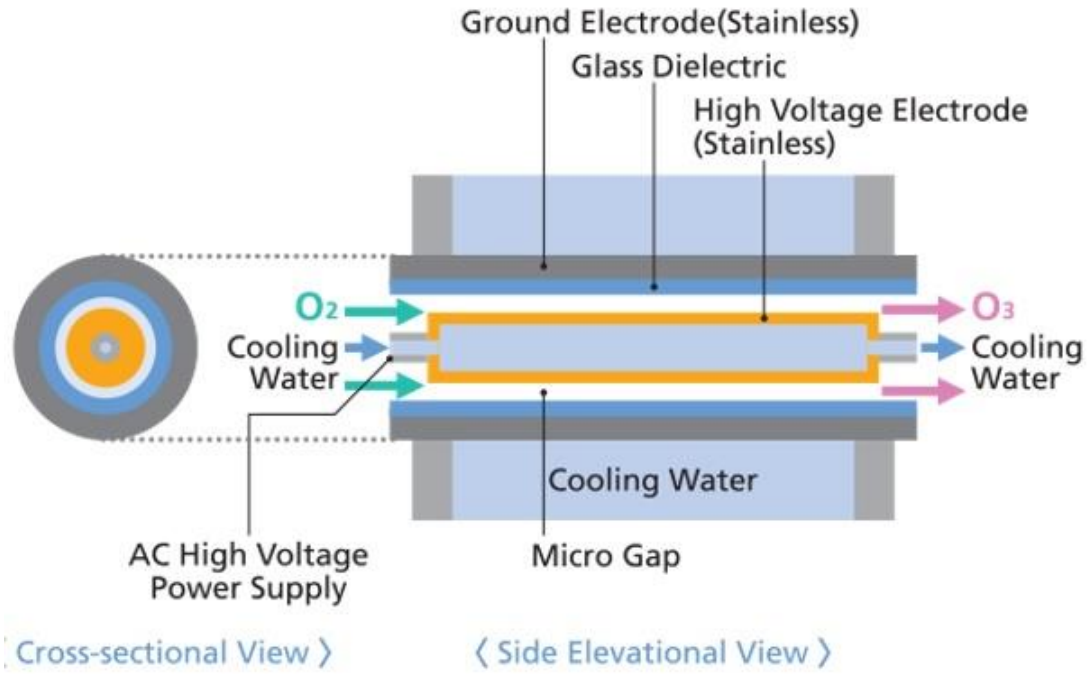

***Figure 3**. Industrial ozone production schematics [4]*

Inside the dielectric – glass tube - is the tubular space where the oxygen current circulates, which is ionized to ozone, dimension of space is 1-2mm. Towards the center is the high voltage electrode in contact with the high voltage AC source, which supplies the installation, also made of stainless steel. This electrode is hollow on the inside and is cooled by a stream of water, connected with electrically insulating silicone hoses. This installation is suitable for "lightly" polluted waters, groundwater influenced by surface waters, lakes, "light pollution" infiltration into the waters.

For more heavy pollution, a scheme with 2 levels of ozonation and filtration is used, and a 3 level treatment led to drinking water. This installation is suitable for oil-polluted water in lakes, rivers, aquifer water polluted with organic and inorganic pollutants, "heavily" polluted water bodies, thermal waters containing hydrogen sulfide, methane and other substances.

Conclusion: I will use this technology in this work for the depollution of the waters from hydrocarbon products, based on ozone - one of the most powerful oxidizers on earth, at the same time a non-polluting element after the reaction, with special efficiency on reaction, energy and environment.

- *Gas nanobubbles use in polluted water treatment*

Production of nanobubbles with hydrodynamic cavitation plant based on vortex mixing nozzle or dissolution method [5]. The scheme of the installation is that in Figure 4.

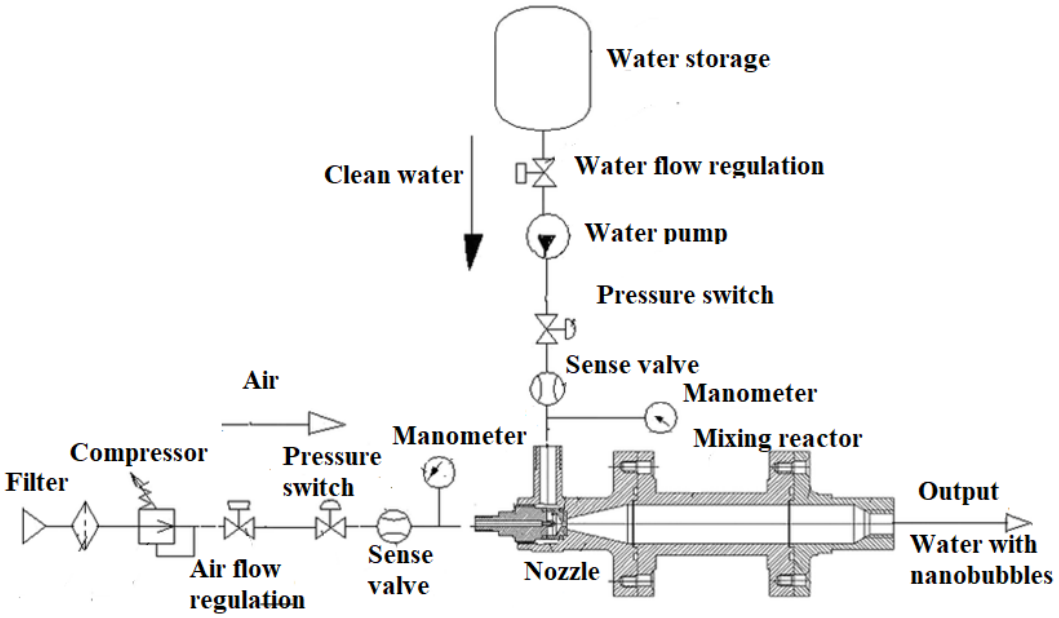

Figure 4. *Nano-bubbles production by vortex or desolute effect schematics [5]*

Consisting of absorbing a gas into a liquid, based on the principles of Henry's law, the concentration of gas absorbed into a liquid depends on its partial pressure. The stages of the process are: the introduction of the liquid at low initial pressure, the pressure increases in the hydraulic circuit, through a vortex or mixer type device, the gas with negative pressure is introduced and is absorbed by the liquid.

The process continues by the static pressing stage of the mixture simultaneously with the reduction of its dynamic pressure and the complete dissolution of the gas into the liquid. Then the mixture is evacuated through a nozzle that increases the efficiency of mixing, transforming the liquid into a saturated liquid-gas compound, according to Figure 5.

The installation is based on the cavitation property achieved by the rotating nozzle of the water jet that absorbs the gas jet, followed by the combination of constituents in the mixing chamber. The process depends on the type of gas applied, the ratios of gas-to-liquid quantities, the pH of the solution. It is an efficient process to be used especially for the flotation properties of the components, in the case of the separation of the elements of different density.

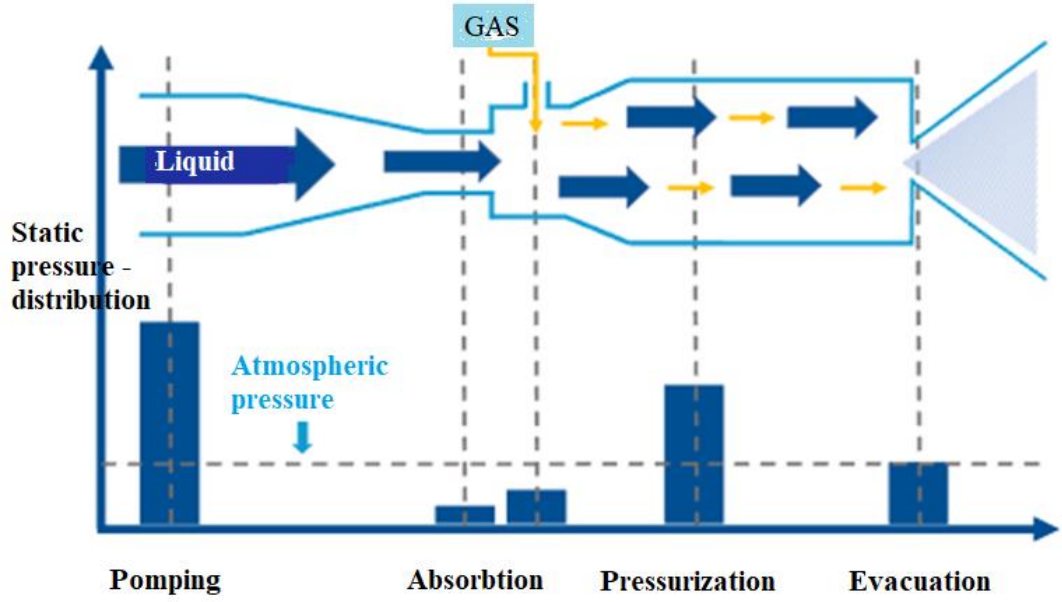

***Figure 5**. Diagram of the nanobubbles by dissolution production process [6]*

2. Treatment of hydrocarbon-polluted waters with nanobubbles of oxygen, ozone and nitrogen

The generation of gaseous particles – bubbles – is a static or quasi-static process. Interacting bubbles fuse and merge in large bubbles.

The most advantageous treatment of hydrocarbon -polluted waters turns out to be, after separation from inorganic matter and solid parts of hydrocarbons, with ozone and oxygen in the form of nanobubbles, mixed initially in clean water and then inject in polluted water. The installation shall be supplemented by a reaction vessel, where the liquid stagnates the reaction time required for the separation or destruction of hydrocarbons, while depending on the temperature, pressure of the liquid, the degree of load and the type of pollutants. After the reactor, the water is filtered primary. If necessary, the plant shall be completed with an additional ozone reaction floor and a new, lower resolution filter of zeolites or coal. Depending on the desired result, water for the resumption of the production process or disposal in the emissary, the installation is carried out in 2 levels. If the target is agricultural or drinking water, the plant shall be completed with an additional ozone or oxygen reaction floor, an ultraviolet ozone destruction reactor and a carbon filter or fine zeolites.

Oxygen and nitrogen are obtained by separating the air into a zeolite medium, as described at the beginning of this article. Thus, from a volume of air, 21% is oxygen O_2 and 78% nitrogen N_2 with a degree of obtained purity of 90-95%.

Ozone O_3 is obtained from energization at high voltage and low frequency of the oxygen. By using the audio frequency, the voltage level required to obtain the same amount of ozone is reduced. In water, ozone is highly soluble and produces OH^- radicals, which make it very reactive. As a result of the reaction, ozone breaks down in water in O_2, which leads to additional oxygenation of the water, but also to OH^- radicals, which make it very reactive, less than ozone.

The next gas as reactivity in water is air, which has a proportion of 21% oxygen, that produces OH^- radicals. Of the 4 gases, the least reactive gas is N_2 nitrogen, and the least soluble in water. The use of nitrogen nanobubbles in water is useful for cleaning hydrocarbon dirty equipment and installations. Even glued to the surfaces, petroleum products are detached by the jet of water with nitrogen nanobubbles, due to the infiltration of nitrogen in the presence of water through the smallest cracks, pores of the hydrocarbon, followed by an increase in distance between the edges of the crack - like a crowbar - due to the coupling of the nanobubbles into larger bubbles, which leads to the detachment of the hydrocarbon parts from the surfaces. Nanobubbles technology facilitates the dissipation of ozone gas into water [7].

Dissolved oxygen (DO) concentrations of 5 ppm were obtained in polluted waters, following treatment, with simple machines and reduced energy consumption. The effect was the separation of oil waste from water, both solid and liquid. The oxygen and air nanobubbles in clean water have been verified to be stable for up to 3 and 5 months respectively, without significant changes in size and electrical potential. [8].

The treatment with oxygen nanobubbles of the wastewater lake is presented in the graph in figure 6 with the parameters of oxygen concentration in water, BOD/COD concentration before installing nanobubbles equipment. [9, 10]

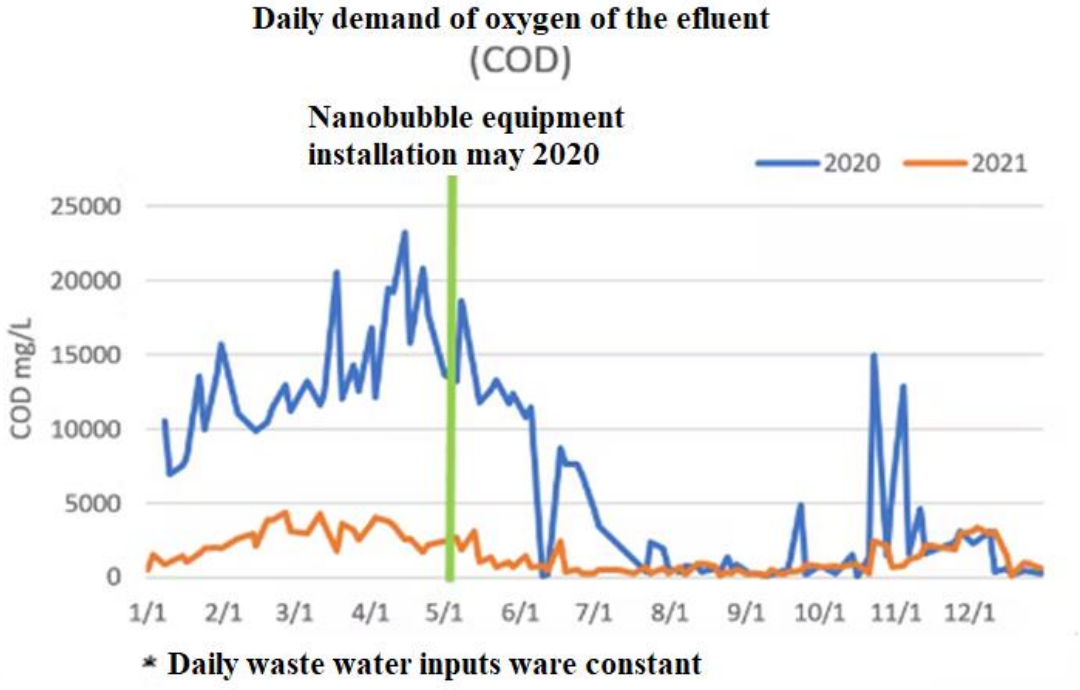

***Figure 6**. Graph of oxygen necessity before and after nanobubbles installation [9]*

The effect was long term increase degree of oxygenation of the waters, the reduction of the mud on the riverbed due to the aerobic digestion of bacteria and the return of the small living creatures in the place, thus the greening of the location. Figure 6 shows the varied graph of oxygen uptake [9]

3. Presentation of the hydrocarbon-polluted water treatment system by oxygen and ozone nanobubbles technology

The system that this work considers to best respond to the hydrocarbon water treatment application is the one with solid separation and large hydrocarbon components, complete with ozone and/or oxygen nanobubbles, combined with devices for increasing the reactivity of the components by vortex effect, static mixer, permanent magnets and eventually ultrasonic treatment.

The simplified schematics of the water treatment plant with ozone or oxygen nanobubbles through vortex tube with nozzle and static mixer is shown in Figure 7.

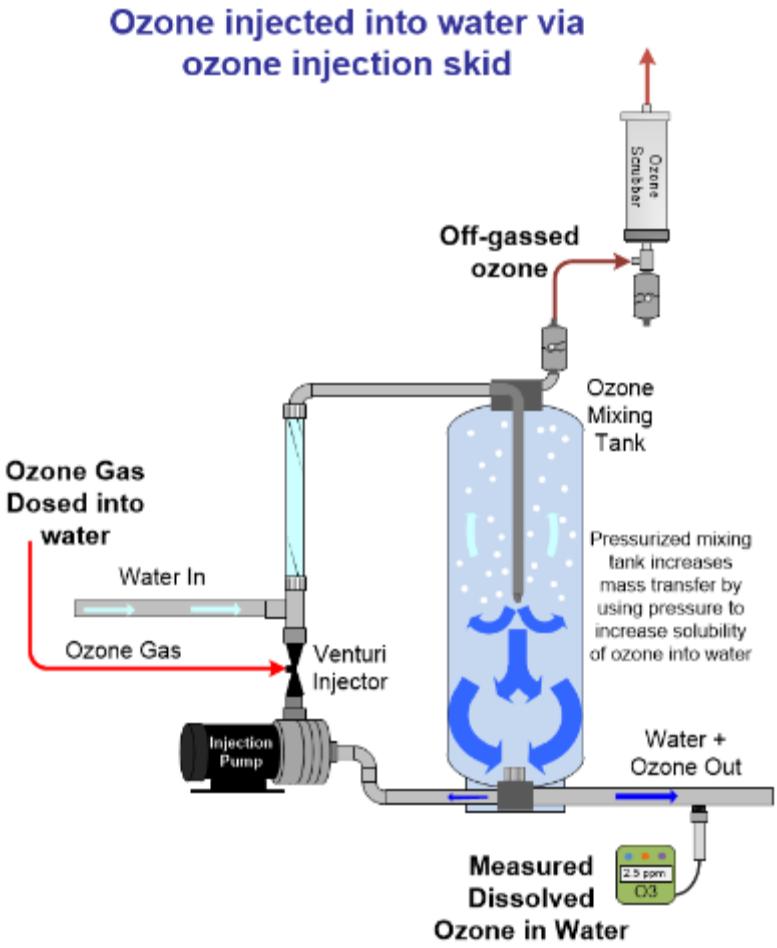

***Figure 7**. Nanobubbles treatment of polluted water schematics.*

The treatment plant for polluted water after the inorganic fraction of raw polluted water and recyclable hydrocarbons has been extracted, is shown in Figure 7. The water pump extracts clean water from the reactor basin, which is mixed with the ozone from the oxygen & ozone plant by the vortex tube with the nozzle and the static mixer. The resulted liquid with ozone nanobubbles is introduced into the reactor vessel where it is mixed with polluted water. The reaction of ozone – pollutants take place, resulting in clean water extracted at the exit of the reactor, after measuring the dissolved ozone. If it is above the

standard quantity, the plant shall be completed either with filters or with a UV installation for excessive ozone annihilation.

4. Application: hydrocarbon polluted water treatment installation based on separation and ozone/oxygen nanobubbles technology

For a hydrocarbon-polluted water treatment capacity of 3.2 m^3/h, the treatment plant is composed of the following:

- The supply pump at the level of the line is 4 m^3/h. For the continuity of the process, the inlet pump must be doubled for having one in "hot reserve".
- Separator of inorganic matter and solid hydrocarbons, possibly recyclable liquids. This equipment makes the gravimetric separation of the inorganic materials driven by the feed pump – sand, metal oxides, coal or earth – that settle on the bottom of the device in a first section. These solid materials are periodically discharged into the drain store, from which the drained water is returned to the separator. The solids are 3-10% of the initial input and can be extracted with specialized pneumatic or hydraulic system. Section 2 of the separator treats the water with hydrocarbons for the separation of the recyclable fraction of hydrocarbons from the water at the level of 95% (5% water) by the technology presented in this paper.
- From the separator, the water is mixed with the nanobubbles solution. The nanobubbles solution is clean water taken from the line outlet, in which, through a nanobubbles-producing Venturi tube, water is mixed with the working gas - ozone and/or oxygen. As hydrocarbon pollution is intense most of the time, ozone will be used.
- The installation for the production of oxygen by separation from the air, based on lithium zeolites, will produce for the exemplified capacity an amount of 5-6l/min of oxygen at a purity of 93-95%. The electric consumption for the production of this amount of oxygen is 220-280W.
- The oxygen produced feeds the ozone plant, which supplies 18-20 g/h. For waters with a low pollutant load, an ozone concentration of 4 g/m^3 is used. The high hydrocarbon load can lead to doubling the concentration of ozone. The solubility of ozone in water at a pressure of 4 bar and the temperature of 15ºC is 104 g/m^3 of water. The electrical consumption of the ozone production unit is 200-250W.
- The ozone water pump, which mixes the solution with nanobubbles, is on DN40 mm, of power 1-1.5kW, at a pressure of 4 bar and has a flow rate of 35 l/min.
- The vortex tube with the nozzle must be on DN40 mm, with reduction in the diminished area to DN22, the slope towards reduction is 25º, the reduction of length 22 mm and the slope from reduction to DN40 of 7º. The static mixer is DN40 mm. The gas inlet is on the diameter of 6 mm.
- The reaction basin must provide at the temperature of the polluted water – e.g. 15ºC -, the reaction time of 10 minutes, so it will have a minimum capacity of 350l.
- Filter 1 of 20" size can be sand or zeolite matter, on DN40mm.

- The reaction basin 2 with ozone, if necessary, is of 5 minutes reaction time, of 180l minimum.
- Filter 2 size 20", if necessary, is 5-20 microns.
- If the UV lamp is required, it must be DN40 mm, 25-36W.

The block scheme of the installation proposed by this work is shown in Figure 8.

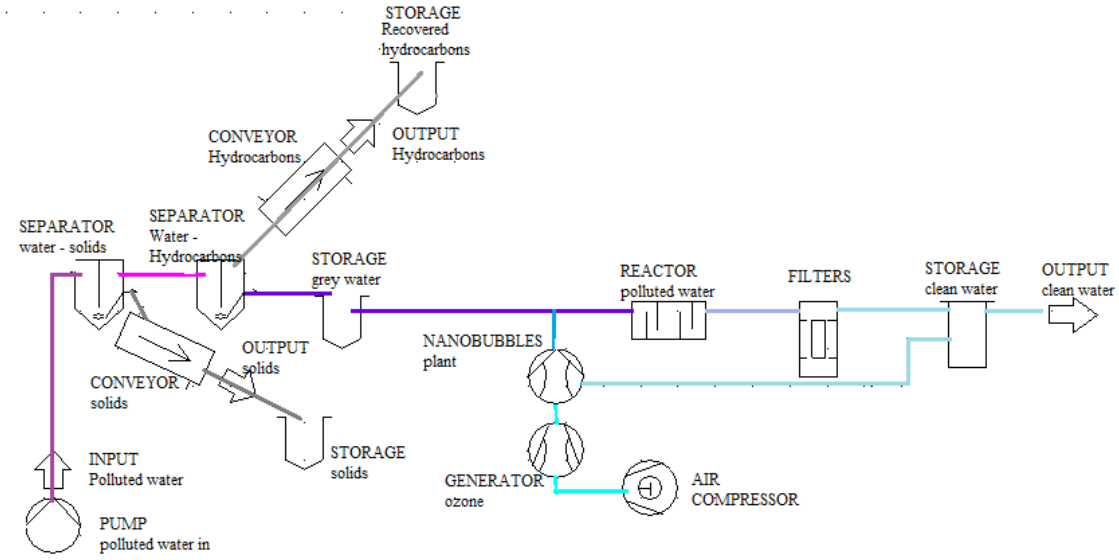

***Figure 8**. Schematics of hydrocarbon polluted water treatment installation*

RESULTS AND DISCUSSIONS

The application presented is the treatment of the hydrocarbon polluted water installation for washing of barges and containers transporting fuel or petroleum products. The resulting water has the necessary and sufficient composition for the resumption in the technological process without additional treatment, without being exchanged for fresh water. The plant does not process the oil waste, which will be transported to a unit specialized in this operation.

The plant operates in a closed circuit, starting from clean water, loaded with nitrogen nanobubbles – to facilitate the detachment from the walls of the barge or the transport wagon of the attached petroleum products. It is then discharged with the pump to the primary separation basin of solid particles and heavy hydrocarbons.

The nanobubbles plant, powered by an air compressor, introduces the ozone nanobubbles into the water after the first separation, followed by the treatment in the second container – the reactor, where the light hydrocarbon fraction in the water is also separated. Light hydrocarbons are collected and discharged into the hydrocarbon container, and the resulting water, released by hydrocarbons, is treated with ozone again in a second reactor, after which it is fed to the high-pressure pump for the resumption of the circuit for cleaning the walls of the barge/wagon.

CONCLUSIONS

- There is no single solution for the treatment of hydrocarbon-polluted waters. The solution is chosen following the evaluation of the situation, of the polluting components, of the weights of the components in the volume of polluting hydrocarbons, of the polluted water body, of the volume of water relative to the volume of pollutant, of establishing the final result of the water body, of the intended budget;
- Depending on the type and volume of polluting hydrocarbons in the volume of infested water, it is decided either to separate and recycle the hydrocarbon or to destroy it within the treatment process. The separation and recycling of hydrocarbons into energy, or hydrogen, becomes interesting when the resulting volumes of hydrocarbon are important, from hundreds of kg upwards;
- Based on these technologies – ozone, oxygen, nanobubbles – one can make water treatment plants polluted with hydrocarbons, separating hydrocarbons and recycling them in separate circuit, with finality in obtaining clean water to resume the technological process, or to return it to nature, or, following a more complex process – to make it suitable for agriculture and even human consumption;
- The study proposes a feasible installation under the conditions of the author, as well as the use of techniques and related equipment for increasing the degree of recovery of polluting hydrocarbons, of separation with high efficiency and high purity of water hydrocarbons, of water treatment from hydrocarbons of hydrocarbons or other polluting components in water, to the level of water viability for return to the water body, or more complex, for its use for agricultural, drinking purposes.

Thus:

- when the polluted water enters the treatment plant, the separation of the solid fraction driven by the polluted water will be made – by depositing on the bottom of the separator container the solid particles, periodically discharged through the solid transport installation – made with a screw conveyor or a valve conveyor.
- The separation of light hydrocarbons from the water will be achieved with a unit described above– absorption at superficial level, through depression, with propeller pump, followed by separation with turntables. When the container is loaded, the direction of the propeller changes to evacuation of the hydrocarbon into its processing circuit.
- Water treatment, released of hydrocarbons and solid particles, will be with ozone and/or oxygen nanobubbles into the reaction tank.
- Filtration of treated water from reaction residues and storage in the clean water container for final analysis and release into the emissary.

REFERENCES

[1] https://www.surfcleaner.com

[2] https://www.gsamaras.gr/en/product/6/oxygen-nitrogen-generators/24/oxygen-nitrogen-generators

[3] https://www.gsamaras.gr/en/product/6/oxygen-nitrogen-generators/24/oxygen-nitrogen-generators

[4] Moleaer (www.moleaer.com)

[5] Levitsky I., Gitis V., Tavor D., The Generation of Coarse Bubbles and Flow Instability Control by Means of Novel Bubble Generator, March 2019, Chemical Engineering & Technology, DOI:10.1002/ceat.201800158

[6] Innovative technologies for nanobubble generation, Acniti, 2022, https://www.acniti.com/technology/nanobubble-generation/

[7] Meegoda J.N., Batagoda J., A New Technology to Decontaminate Sediments Using Ultrasound with Ozone Nano Bubbles, Geo-Chicago 2016, pp. 392-401, DOI: 10.1061/9780784480168.039

[8] Alam H.S., Sutikno P., Soelaiman T.A.F., Sugiarto A.T., Bulk Nanobubbles: generation using a two-chamber swirling flow nozzle and long-term stability in water. Journal of Flow Chemistry, 12, 161–173, 2022. https://doi.org/10.1007/s41981-021-00208-8

[9] White A., Case study: Nanobubbles reduce BOD/COD concentrations in food processor's wastewater lagoon, Dec. 6, 2022, https://www.watertechonline.com/wastewater/article/14285689/case-study-food-processor-wastewater-lagoon-nanobubbles-reduce-bodcod-concentrations

[10] Lim S., Shi J.L., von Gunten U., McCurry D.L., Ozonation of organic compounds in water and wastewater: A critical review, Water Research, Elsevier, 2022, https://doi.org/10.1016/j.watres.2022.118053

Received: May 2023; Accepted: June 2023; Published: June 2023