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Piotr Robert WILIŃSKI* and Jeremi NAUMCZYK

Faculty of Environmental Engineering, Warsaw University of Technology, Nowowiejska 21, 00-653 Warszawa, Poland
(* Corresponding author, e-mail: piotr.wilinski@is.pw.edu.pl)

Abstract

The lack of fresh water is one of the major threats for people. The extremely sufficient and cost saving methods for water and wastewater treatment must be applied. The paper shows possibility of using traditional Dissolved Air Flotation method (DAF) with alternation of feeding gas by ozone (Dissolved Ozone Flotation – DOF) instead of air to obtain better treatment results and possibilities of decreasing the costs of water and wastewater treatment. Moreover the DOF method may come in effective in case of more and more restrictive recommendations regarding water quality and micro-pollutants removal. As the method is on early stage of the research many technical aspects and mechanisms must be taken into consideration and to be investigated. Presumably the DOF method could be applied in technical scale for pre-treatment of industrial wastewaters, fracturing fluids, water with algae or for final separation of effluent and excess sludge in municipal wastewater treatment plants.

Keywords

dissolved air flotation (DAF); ozonation; water and wastewater treatment, industrial wastewater

INTRODUCTION

Nowadays, the lack of freshwater impels governments to create new, more restrictive law and private companies to create new, sufficient and cost- and energy-effective technologies and methods for purification of water and treatment of wastewater. The shortage of freshwater can be seen especially in Asia (fast growing population) and Africa (lack of freshwater reservoirs). Poland has problem with limited amount of freshwater. In many cases it is bad quality water. All in all, this issue has high importance, as water (clean freshwater) is at the bottom of human's life.

Flotation method is mainly used in two sectors: mining industry (for separation of metal ores) and in wastewater treatment process (both for municipal and industrial wastewaters) for separation of suspended solids, emulsions, chemical sludge or excess sludge. Conventional flotation relies on floating of solids (mainly suspended solids) on the top of the liquid by air bubbles (in conventional process they have and average diameter of 100 – 300 μm). Better separation effect is obtained when air bubbles are very small (micro and nano). Special dispersing pumps are able to create air-water mixture of nanobubbles and process is named as micro- and nanoflotation. Coagulants and flocculants are used in the process for better agglomeration of small particles and colloids. Ferrous or aluminum sulfates are the most common coagulants and they are mixed with water or wastewater before entering flotation unit.

Nowadays, micro and nanoflotion with ozone (Dissolved Ozone Flotation, DOF) is in laboratory research scale. The research is conducted mainly in Asia: South Korea (Ulsan University), Japan (Kyoto) and China (Xian). However it is very early stage of the research. In this method ozone is used instead of atmospheric air. This substitution causes ability to obtain two processes in one unit: separation of solids and emulsions by gas bubbles (as in conventional flotation) and oxidation of soluble organic compounds using strong oxidizing agent – ozone. Synergy of those two processes (separation and oxidation) can lead to better treatment effects. It can cause positive results as: decreasing dosing coagulants and flocculants, pathogen removal, improvement of wastewater biodegradability, micro-pollutants removal (antibiotics, hormones, personal care products), decreasing the amount of excess biological sludge (in case that DOF unit is used for separation of effluent from excess activated sludge).

Previous research was focused on process efficiency, but only relationship between dose of ozone and treatment efficiency was measured. It must be mentioned that in the past research, the conventional flotation (coarse bubbles) was implemented (not micro – nanoflotation with bubbles size of 1-20 μm). Thus, in the research essential fact was omitted. The size of bubble has enormous influence on kinetics and efficiency of oxidation process. The main parameter which can limit the process kinetics is mass transfer of ozone into the solution (wastewater). The efficiency of the process depends on total area of ozone bubbles in the solution. The bigger area (the amount of bubbles generated) causes higher mass transfer kinetics of ozone and velocity of organic compounds oxidation is increasing. In conclusion, this problem can be solved using appropriate air dispersing pumps (micro- and nano-bubbles pumps).

Until now, the research on conventional flotation with ozone as feeding gas was made on municipal, livestock wastewater and as the method of tertiary treatment. During testing of municipal wastewaters, LEE *et al*. (2008) observed the higher efficiency of the process for DOF method comparing with conventional DAF in case of reducing: suspended solids, color, Biological Oxygen Demand (BOD), turbidity, total phosphorus. Additionally, the great effect of disinfection and removing coliform bacteria was noticed. LEE *et al*. (2006) made the research on livestock wastewater. The effects were as well good considering the reduction of suspended solids and Chemical Oxygen Demand (COD). JEAONG *et al*. (2011) claimed, for pigment wastewater, efficiency of DOF method combined with sequencing batch reactor (SBR). Separate SBR and DOF-PO_2 method did not fulfilled the discharge limits. After combining both methods required limits were obtained.
The DOF method was tested by YA-LING et. al (2010) for checking the ability of algae removal from freshwater. Small amount of ozone in feeding gas gave positive effect of algae cells agglomeration and better flotation on the top of the solution afterwards.

As DOF method is new and innovative technology, many questions appear and must be answered. The aims of the research (first year of ongoing PhD study) are following:

- to examine the effectiveness of a combination of two processes: micro- and nanoflotation with ozonation,
- to examine technical and operational factors affecting the process (bubbles size, pH conditions, coagulant and flocculant addition),
- to examine treatment efficiency of the DOF process compare to DAF process in case of treatment fracturing fluids, industrial wastewater and water containing algae,
- to choose trace micro-pollutant (i.e. biocide in used fracturing fluid) and check its removal efficiency by DOF with comparison with DAF method,
- to examine the potential reduction of operating costs and treatment efficiency,
- to research the influence of ozone on potential increase of wastewater biodegradability.

MATERIAL & METHODS

Testing method

Dissolved air flotation unit with the volume of 150 L (active volume) was used as testing unit. Air dispersing system was supported by micro-nano bubble pump Karyu Turbo Mixer15NPD (KTM Nikuni Pump). The pump has mixing tank for preparation of air-water feed. Ozone was generated by BNP Ozone-Generator S0Z-Y0B-10G (power 400W, ozone output 10g/h) and connected to KTM pump to generate air-ozone-water mixture. Flocculants and coagulants (Iron (III) sulfate) used in DAF process were dosed directly to the reactor.

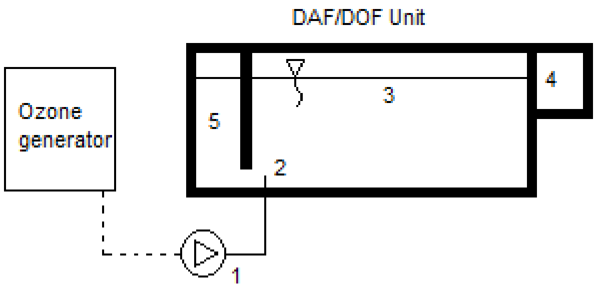

Figure 1: Dissolved Air (DAF) and Dissolved Ozone Flotation unit scheme: 1 – Nikuni Pump, 2 – air-water mixture injection, 3 – main flotation unit tank, 4- sludge tank, 5 – clean water tank

Collection of samples

After pilot tests of DAF and DOF methods, influent and effluent samples (1,0 dm^3) were collected for chemical analysis. At the moment only one test was made at the fruit processing factory. The test was conducted to check-up and compare pre-treatment efficiency of DAF and DOF method and to calculate possible reductions of the cost on the biological step of wastewater treatment. Further tests (i.e. on fracturing fluids for checking micro-pollutants removal efficiency) will be made during ongoing PhD research.

Chemical analysis and process parameters analysis

Laboratory analysis was conducted to obtain the values of: COD, BOD_5, Total Suspended Solids (TSS), pH.
In further analysis other parameters will be measured: Total Organic Carbon (TOC), biodegrability, toxicity, selected micro-pollutants concentration decrease (by HPLC).
Also process parameters will be measured: bubbles size (ozone mass transfer), optimum ozone concentration, process kinetics, coagulant and polymer dosage.

Design of dimensions of biological treatment step

ATV-DVWK method was used for dimensioning of biological step after DAF and DOF pre-treatment and show how each method influence next treatment step. The calculation was made based on organic matter removal (without nitrification and denitrification processes).

RESULTS AND DISCUSSION

Fruit processing wastewater

The test was made at the fruits processing factory (apples). The factory produces apple's concentrate. The average daily wastewater flow is Q_d= 1 400m^3/d (wastewater from production). The plant has own mechanical-biological WWTP. However the owner wants to enhance the treatment efficiency, especially before biological step (by reduction of loadings on biology). Wastewater for analysis was taken from sewer with wastewater from production.

The experiment procedure and results

Flotation unit was fulfilled with 150L of wastewater and then flotation process was conducted for 20 minutes in each case (DAF and DOF). For DAF method iron (III) sulfate was used as a coagulant (0.3 mL of iron (III) sulfate)/1 L wastewater) and anionic polymer as a flocculant (2mL of polymer/1L wastewater). The kind of coagulant and flocculant and their quantity were chosen based on author's previous experiences in this kind of industry wastewater and jar tests. In DOF method coagulant was not dosed. Instead of air-water mixture for flotation (in traditional DAF method) air-ozone-water mixture was used. Ozone was used in quantity app. 3,5g/run of DOF test. The amount of anionic polymer added was 1.5 mL/L of wastewater.

In table 1 are collected results from DAF and DOF tests and raw wastewater. Wastewater pre-treatment efficiency was measured for each method (DAF and DOF) twice. The results in table 1 are average from two measurements. Higher treatment efficacy was observed for DOF process compare to DAF. The COD, $COD_{soluble}$, BOD_5 concentrations are lower in the case of DOF unit effluent, 33.8%, 29.3% and 34.8% respectively compare to 20.1%, 6.6% and 20.3% in case of DAF unit. Those results were used for calculation of possible exploitation costs reduction in the next paragraph.

Table 1: Parameters comparison for influent wastewater and effluent after DAF and DOF process for fruits processing industry (average from two measurements)

Parameter	Unit	Influent	After DAF [% removal]	After DOF [% removal]
COD_{total}	mgO_2/dm^3	4 080	3 260 [20.1]	2 700 [33.8]
$COD_{soluble}$	mgO_2/dm^3	3 310	3 090 [6.6]	2 340 [29.3]
BOD_5	mgO_2/dm^3	2 270	1 810 [20.3]	1 480 [34.8]
TSS	mg/dm^3	930	310 [66.6]	510 [45.2]
pH	-	9,0	8,0	8,8

The figure 2 shows colour difference between raw wastewater and wastewater after DAF treatment. The next figure (no 3) shows DAF and DOF pilot-test unit during the test in factory.

Figure 2: DAF effluent and raw wastewater during tests

Figure 3: Dissolved Air Flotation (DAF) and Dissolved Ozone Flotation (DOF) unit during tests

<u>Biological treatment step dimensioning and hypothetical exploitation costs reduction</u>

The design procedure was conducted to compare influence of using ozone in flotation process on biological treatment step. It led to show merits of DOF process comparing with DAF as a pre-treatment method before biological treatment.
Biological step dimensions for DAF and DOF as pre-treatment step were calculated based on ATV-DVWK method. The design was made for 15°C and calculated basing on COD loading. For the air distribution system, air grid with diffusers (fine bubbles) was designed. The reactor high was assumed as H=6.0m.
The results are shown in table 2.

Table 2: Biological step dimensions for DAF and DOF as pre-treatment method (calculations for wastewater temperature T=15°C)

Parameter	Unit	After DAF	After DOF	% reduction for DOF compared to DAF
Reactor size	m^3	3 807	3 587	5.8
Oxygen demand	kgO_2/h	105.2	129.0	18.5
Air demand	Nm^3/h	3 150	3 870	18.6
Energy demand for aeration (air blower motor power)	kWh	110	130	15.4
Excess sludge production	kg/d	1 816	1 648	9.3

The results obtained from ATV procedure shown significant reduction of exploitation area, oxygen (air) demand, sludge production and energy demand by using DOF instead of DAF.
For the results from table 2 yearly exploitation savings were calculated. Working year was assumed as 250 days (24h/d operation) and for 1 400m^3 of wastewater flow. The following savings were calculated:

- 21 500 €/ year – by reducing usage of iron (III) sulfate,
- 3 500 €/ year – by lower sludge production,
- 10 800 €/ year – by lower energy consumption by air blower,

Obviously cost of the ozone generation must be subtracted from total savings. However the cost of ozone generation amount to only 17% of iron sulfate dosage. In total savings are calculated as ca. 32 000 €/ year. This value is approximated, however it gives positive and prospective sight of DOF technology and reasons for further research.

CONCLUSIONS

As previous results obtained by Lee (2006), Jin (2006), Cheng (2010) and others and first experiment made by author at fruit processing plant showed promising effects, consecutive experiments must be carried on. Further laboratory research will be focused on DOF process efficiency for treatment of: fracturing fluids from shell-gas exploitation process (concentration reduction of selected micro-pollutant i.e. biocide), selected industrial wastewater (i.e. cosmetics wastewater) and water containing algae. The most important questions regard process kinetics and mechanism, factors affecting process and merits and demerits of DOF method.

It cannot be omitted that there are threats which may discontinue research on DOF method. One of the major thread is organic micro-pollutants and chemical compounds transformation by ozonolysis process. There is no information about the research on this process regarding wastewater. On the beginning of nineties the similar problem appeared regarding ozonation of potable water in case of bromines. As those ions are considered to be cancerogenic, many researchers focused on the formation of bromines and reaction mechanisms. Biń et al. (1999) underlined the problem and showed the further difficulties which could appear i.e. in case of modelling of bromines formation and proper technology application and design. The similar objections should be considered during DOF research in this PhD thesis. In consecutive research toxicity tests would be applied to check how the DOF process can affect wastewater's influence on life forms. As DOF process may be used as a pre-treatment step before biological treatment, some concerns may rely the influence of residual ozone on microorganisms of activated sludge (bacteria). However the research made by LEEUWEN *et al.* (2009) showed curious and a bit surprising results. LEEUWEN examined ozone impact on bacteria presented in activated sludge. The research focused on ozonation as a pre-treatment method combined with biological stage and its influence on further biological treatment. From LEEUWEN research it can be seen than ozone had positive effect on microorganisms and treatment efficiency. The concentration of 16.7 mgO_3/L caused proper biological treatment and increased biodegrability of onerous chemical compounds (methylene blue). Moreover the bacteria were not harmed by strong oxidant. Ozone caused selection of microorganims, but it had positive effect on the activated sludge population.
Another threat or strong conviction is the price of ozone generation. It can be seen that over the years new ozone generators are manufactured. The new generators can produce up to 20% of ozone by weight (Primozone), whereas few years ago it was around 12 %. Other important factor is mentioned before micro- and nanobubble system which enables better ozone transfer into the surrounding medium (wastewater).

General efficacy of DOF process was checked. Consecutive research will be done in new laboratory flotation unit designed in purpose of this PhD thesis. Synthetic fracturing fluid will be produced and then treated in DAF/DOF unit. Further laboratory test would be focused on checking process efficiency in case of removal selected micropollutants i.e. biocide, wastewater toxicity and process parameters.

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