Catalytic Ozonation Based Advanced Oxidation Process for Effective Treating Wastewater from Hospital and Community Health Centre Facility by FLASH WWT Catalyst System in Indonesia

R Rame¹, H Pranoto², RKK Winahyu², M Sofie³, BH Raharjo³, AS Utomo³

¹Center of Industrial Pollution Prevention Technology, Jl. Ki Mangunsarkoro No.6, Kota Semarang, Jawa Tengah 50241,
²Bartec Utama Mandiri, Semarang - Indonesia
³Academy of Electrical Medical Engineering (ATEM) Semarang - Indonesia

email: rame@kemenperin.go.id

Abstract. Wastewater from hospital and community health centre facility can contain hazardous chemicals and harmful microbes such as viruses, multi-resistant bacteria to medical contrast agents and chemicals for treatment. Other country has placed pharmaceutical products on substances that be regulated in hospital effluent. The FLASH treatment plant involves physical and biological pre-treatment, followed by Advanced Oxidation Processes (AOPs) based on catalytic ozonation and followed by granulated activated carbon (GAC) and powdered activated carbon (PAC) filtration. Two dominant oxidants are present in ozonation applications: ozone (O³) and hydroxyl radicals (HO'). Hydroxyl radicals are a highly reactive decomposition product of ozone and represent the main oxidant in AOPs. Conventional ozonation, both ozone and hydroxyl radicals can act as oxidants. In AOPs, hydroxyl radicals represent the primary transformation mechanism. Different ozonization types for treating wastewater from hospital and community health centre facility were considered and reviewed, and FLASH as the most common and efficient processes were discussed. In year 2015, 140 FLASH have been applied and gave satisfaction result for 100% effective meet the quality standard from regulation Ministry of Environment of Republic Indonesia for waste water quality standards Number 5/2014. FLASH treatment system could have great significance for hospitals and Community Health Centre Facility in Indonesia that face problems as removing micro pollutant. BUMA FLASH treatment is the first develop hospital wastewater treatment in Indonesia based Catalytic Ozonation Based Advanced Oxidation Process.

Keywords: catalytic ozonation, AOPs, wastewater, hospital Indonesia
1. Introduction
Wastewater from hospitals can contain hazardous chemicals and harmful microbes such as viruses, multi-resistant bacteria to medical contrast agents and chemicals for treatment [1-4]. But now a FLASH full scale plant in Indonesia has removed these residues, potentially addressing a hospital wastewater problem. The issue of hospital wastewater being sent to public sewage treatment facilities is a major problem. Municipal sewage treatment plants using conventional treatment are not designed to deal with medicinal and toxic waste [5-6]. This caused detection these substances in surface water. Hospital wastewater can pose a health hazard to humans, especially employees at wastewater treatment plants. During heavy rains and flooding, holding tanks in the sewer system can overflow and expose the public to these hazards [8]. There is also a danger to aquatic life. Once the sewage is treated and released into the environment along with its residual content of pathogens and pharmaceuticals, the local flora and fauna are routinely at risk [9].

Even in very low concentrations, the substances in hospital wastewater can affect environment. Estrogens [10], for example, can cause hermaphroditic fish, while some painkillers [11] are poisonous to fish. Hospital wastewater and household wastewater are treated in the same way and that’s not a very effective approach in Indonesia. Meanwhile, the European and other countries has placed pharmaceutical products on substances that be regulated in hospital effluent [12-14]. However, there isn’t Indonesia standards regulation for pharmaceuticals or pathogens in hospital wastewater. To deal with the wastewater issue, the national company of BUMA (Bartec Utama Mandiri), established an innovation in treatment hospital wastewater that involved sending the hospital effluent at much closed through FLASH, a series of treatments. FLASH full-scale hospital and community health centre waste water Treatments in Indonesia from different province have been adopted and investigated.

The goal of FLASH Treatments was to find a solution that actually removed the problematic substances in hospital wastewater rather than simply diluting it with other wastewater streams in the public treatment system. The result was a compact, tailor-made wastewater treatment plant designed by BUMA. Local on-site treatment of wastewater is key to the success of the system. FLASH plant receives wastewater directly from the hospital. It is not mixed with the water from the public wastewater treatment system. This makes it possible to specifically target the substances in hospital wastewater.

![Figure 1. FLASH Full-Scale WWT.](image)

The FLASH treatment plant involves physical and biological pre-treatment, followed by Advanced Oxidation Processes (AOPs) based on catalytic ozonation and followed by granulated activated carbon (GAC) and powdered activated carbon (PAC) filtration units as shown on Figure 1. This treatment system is extremely flexible. Each unit can be expanded, removed or adjusted to accommodate changing needs. The physical layout of the plant is also fundamentally different from conventional wastewater facilities. Wastewater from hospitals is typically fed into large, municipal treatment plants that take up a lot of space and require long pipelines from the hospital to the treatment plant in Indonesia. BUMA
developed FLASH a compact water treatment plant that can be delivered in three or four prefabricated modules. It’s no bigger than a small room and it enables hospital wastewater to be treated locally and then safely released into the local environment.

BUMA will continue to encourage hospitals and community health centre in Indonesia to apply FLASH treatment to get some benefits, namely optimal treatment efficiencies, operational cost and optimal combination of ozone and granular/powder activated carbon. During FLASH treatment, the treated water can be re-used locally as technical water at the hospital and some will be released directly into the nearby environment/river, where it will contribute to a more stable water flow. In other words, the water that was once a risk can in future become a resource.

FLASH treatment system could have great significance for hospitals in Indonesia that face the same problems as removing micro pollutant. BUMA innovation as FLASH have the solution to a problem that exists at a great many hospitals in Indonesia. BUMA FLASH treatment is the first hospital wastewater treatment in Indonesia to invented and install this advance technology. In the years to come, FALSH technology will become extremely important especially in industrialised province/district where there is a political interest and a focus on the environment.

2. Materials and Methods

Literature were searched with original search terms were used (“Catalytic Ozonation Based AOP,” “Ozone Chemistry,” “Ozonation of micro pollutant,” “Ozone-based AOPs, including more terms to search for ozonation (“pathogen” “antibiotic”) from literature database provider such as springer, sciencedirect, and elsevier.

Data from outlet of FLASH full-scale hospital waste water treatments in year 2015 include physical parameters (temperature, dissolved solids, suspended solids), chemical parameters (pH, COD, BOD, oils and fats, MBAS, ammonia nitrogen, heavy metals), and biological parameters (total coliform) were collected from BUMA. The results of data analysis are then compared to water quality standards in accordance with their designation stipulated by regulation of the Minister of Environment Republic of Indonesia number 5:2014 about waste water quality standards.

3. Results and Discussions

3.1 Catalytic Ozonation Based AOP

Ozone has recently experienced for treatment of taste and odor compounds,[15] dissolved organic matter (DOM),[16, 17] and emerging contaminants. [18, 19]. Interest in ozone for municipal, industrial and hospital wastewater treatment is continuing to grow at a rapid pace. The spread of antibiotic resistance has become a major global challenge [20]. The emergence of antibiotic resistance has rendered the latest generation of antibiotics less effective since these new antibiotics generally rely on the same fundamental pharmacological mechanisms. Many suggest that the long-term presence of antibiotics in wastewater effluent and finished drinking water may accelerate the spread and transfer of antibiotic resistance genes [21]. To combat this threat, better removal efficiencies for antibiotics in wastewater treatment plants. The ability of catalytic ozonation to remove the threat from wastewater in FLASH is effective and efficient.

The main sources of micro pollutant to the environment are wastewater effluent, bio solids, agricultural wastewater, and manure. Depending on the wastewater composition and the process train of the wastewater treatment plant (WWTP), a range of “removal” efficiencies may be obtained for various micro pollutant. It is important to note that removal usually manifests as partitioning into the solid phase or metabolism/transformation in the aqueous phase. The presence of micro pollutant in bio solids can lead to environmental, and even food crop, contamination. Similarly, metabolites and other transformation products may retain the same pharmacological activity as parent compounds, i.e., the ability to inhibit microorganisms or cause other sub inhibitory effects. For these reasons, it is important to distinguish removal, transfer, and transformation.
One of the early reports of micro pollutants is pharmaceuticals in wastewater focused on measuring 32 drugs in German WWTPs [22]; 80% of the drugs investigated were detected in at least one treatment plant. Much of the corresponding data has been aggregated in several review articles on the presence and fate of PPCPs in wastewater [23, 24]. To date, at least 70 antibiotics have been detected in wastewater. These antibiotics include representatives from various classes, including b-lactams, cephalosporin’s, FQs, lincosamides, macrolides, penicillin’s, sulphonamides, and tetracycline’s, among others. Commonly studied antibiotics include amoxicillin, azithromycin, chlorotetracycline, ciprofloxacin, erythromycin, levofloxacin, norfloxacin, sulfamethoxazole, tetracycline, trimethoprim, and tylosin. These antibiotics are studied more often because their mass consumption tends to be higher than those of others.

As indicated above, antibiotics are not completely removed during wastewater treatment; therefore, antibiotics are present in wastewater effluent and discharged into the environment. The presence of antibiotics in surface waters raises the important question of whether antibiotics are present in drinking water supplies. In this manner, it is clear that surface water concentrations are generally an order of magnitude lower than those detected in raw wastewater. Given the expected dilution of antibiotics on discharge into surface waters, the difference in antibiotic concentrations in raw wastewater and surface waters suggests that WWTPs are the major source of antibiotics in the environment.

Inherently, the presence of antibiotics in surface waters demonstrates that conventional WWTPs do not provide sufficient removal of pharmaceuticals and results in antibiotic contamination of drinking water supplies. While the human health consequences of long-term consumption of trace concentrations of antibiotics are not yet known, eliminating antibiotics from drinking water sources seems prudent especially as antibiotics have been shown to have numerous effects at sub inhibitory levels. Antibiotics are one of the most important classes of pharmaceuticals present in wastewater because of extensive use in hospital.

The contribution of WWTPs to the spread of antibiotic resistance is an increasingly important topic. In the past few years, dozens of studies have identified the presence of antibiotic-resistant organisms and antibiotic-resistant genes in WWTPs, wastewater effluent, and surface waters [25].

Aquatic ecologists have become increasingly concerned about impacts of trace organic contaminants on ecosystems. The continuous introduction of antibiotics into river systems can significantly change microbial communities by favouring antibiotic-resistant bacteria. As microbial communities play an important role in carbon and nutrient cycling, such changes may have drastic effects at the ecosystem level.

### 3.2 Ozone Chemistry

The redox chemistry of ozone demonstrates its effectiveness as an oxidant. Reaction shows the ozone half-reaction as shown on Figure 2.

\[
O_3 + 2e^- + 2H^+ \rightleftharpoons O_2(g) + H_2O \quad E_{\text{red}} = 2069 \text{ mV}
\]

**Figure 2. Ozone half-reaction.**

Ozone is a stronger oxidant than most other traditional oxidants/disinfectants including hydrogen peroxide, permanganate, chlorine dioxide, chlorine gas, oxygen, and hypochlorite. Only hydroxyl radicals demonstrate a greater redox potential \( E_{\text{red}} = 2800 \text{ mV} \).

In solution, ozone undergoes a complex series of decomposition reactions that generate (and consume) other reactive oxygen species (ROS). ROS are exploited in advanced oxidation processes (AOPs), which focus on rapid generation of hydroxyl radicals. Regardless, an understanding of ozone
decomposition is important in the context of ozone-based processes because water quality determines whether ozone decomposition kinetics are rapid or slow. Most importantly, ozone decomposition kinetics affect the ozone exposure achievable for a given applied ozone dose. A direct analogy to ozone disinfection may be helpful as ozone exposure is essentially the CT value.

**Figure 3.** Mechanism of ozonation reactions: (A) directly, (B) catalytic ozonation.

Two dominant oxidants are present in ozonation applications: ozone (O\(_3\)) and hydroxyl radicals (HO\(^\cdot\)). Hydroxyl radicals are a highly reactive decomposition product of ozone and represent the main oxidant in AOPs as shown on Figure 3. Examples of AOPs include chemical (O\(_3\)–H\(_2\)O\(_2\)), photochemical (ultraviolet (UV)–H\(_2\)O\(_2\)), and photocatalytic (UV–TiO\(_2\)) methods, among others. In all these cases, the reaction generates hydroxyl radicals. One important difference between AOPs and conventional ozonation is that during conventional ozonation, both ozone and hydroxyl radicals can act as oxidants as shown on Figure 4. In AOPs, hydroxyl radicals represent the primary transformation mechanism.

**Figure 4.** FLASH Full-Scale WWT.

### 3.3 Ozonation of micro pollutant

In fact, ozone has been successfully used to treat antibiotics in these water sources, as well as specific industrial wastewaters. [27, 28]. Ozone is an excellent choice for removing antibiotics in water and wastewater supplies. Removing trimethoprim, sulfamethoxazole, clarithromycin, erythromycin, and roxithromycin, among others by ozonation of a number of PPCPs in wastewater matrices [27]. With an ozone dose of 5 mg/l found that 95% removal of a suite of seven antibiotics (carbadox, sulfachloropyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole, and trimethoprim) was achieved after just 1.3 min of gaseous ozonation (2% w/w) [29]. Macrolides and sulphonamides were effectively transformed (>95%) in secondary effluent at pH 7 for ozone doses of 2 mg/l. [30]. With an ozone dose of 3 mg/l found that the total mass concentration of 26
pharmaceuticals, including many antibiotics, went from approximately 3800 ng/l to less than 50 ng/l [31]. All of these studies indicate that antibiotics destroy quickly with ozone.

3.4 Ozone-based AOPs
In 1987, Glaze et al. coined the term, advanced oxidation processes, to describe processes that generate hydroxyl radicals [32]. To date, a number of ozone-based AOPs have been described, including the following: O$_3$–HO$_2$, O$_3$–H$_2$O$_2$, O$_3$–UV, O$_3$–H$_2$O$_2$–UV, O$_3$–catalyst, O$_3$–activated carbon, and O$_3$–ultrasound, among others [33–36]. Most ozone-based AOPs exploit the secondary reactant (HO$_2$, H$_2$O$_2$, UV, etc.) to promote ozone decomposition.

![Figure 5. Mechanism of Ozone Decomposition Reactions.](image)

Ozone decomposition result in the production of a number of reactive species such as superoxide anion radicals (O$_2^-$), peroxy radicals (HO$_2^-$), ozone anion radicals (O$_3^-$), hydrogen trioxide radicals (HO$_3^-$), hydrogen tetraoxide radicals (HO$_4^-$), and hydroxyl radicals (HO$^-$) as shown on Figure 5. Hydroxyl radicals are more reactive than ozone, as indicated by their redox potential, 2800 mV. Hydroxyl radicals are often considered nonselective oxidants because the chemical structure and speciation of target molecules does not significantly affect reactivity. For ozone-based AOPs, the ozone exposure is typically minimal because of rapid ozone decomposition and so the majority of treatment from reaction with hydroxyl radicals.

The ideal molar ratio of ozone to hydrogen peroxide is 2 mol O$_3$/mol H$_2$O$_2$. If the molar ratio of ozone to hydrogen peroxide is greater than 2 mol/mol, excess ozone will be present, resulting in a dual oxidant system that first selects for hydroxyl radicals and then ozone as shown on Figure 6.

$$O_3 + H_2O_2 \rightarrow HO^+ + O_2$$

$$H_2O_2 \xrightarrow{hv} 2HO^+$$
Figure 6. Mechanism of O$_3$–H$_2$O$_2$ Decomposition Reactions.

Other ozone-based AOPs, like O$_3$–UV, O$_3$–H$_2$O$_2$; however, the capital costs associated with adding hydrogen peroxide and installing UV lamps are prohibitive. AOPs based O$_3$–catalyst are being increasingly employed [37-44].

Unlike traditional wastewater contaminants like particles, organic carbon, nutrients, and pathogens, these micro contaminants from pharmaceutical and medical industries cannot be easily treated. Therefore, increasing the efficiency of wastewater treatment of contaminants from pharmaceutical and medical industries is in the best interest of worldwide. One approach is adopt of FLASH WWT Catalyst System. By FLAST technology is hopeful that the water treatment pharmaceutical and medical industries will find a solution that enables sustainable stewardship of the environment and maintenance of effective treatment.

3.5 FLASH

Data analysis from thirty-one of parameters which were collected from BUMA such as physical parameters (pH, temperature, total dissolved solids = TDS, total suspended solids = TSS), chemical parameters (COD, BOD, oils and fats, MBAS, Ammonia, iron, Barium, copper, zinc, Hexavalent chromium, Chromium, cadmium, Mercury, lead, Arsenic, Selenium, nickel, Cobalt, cyanide, sulphide, Fluoride, Chlorine free, nitrate, Phenol, Nitrite), and biological parameters (total coliform). Data analysis showed that there were significant difference between values of water from outlet of 140 Flash Full-Scale waste water treatments and the maximum threshold value. Referring to the removal efficiency of macro-pollutants, the collected data demonstrate good removal efficiency of macro-pollutants using FLASH technologies from 140 sampling. The results of the analysis of the thirty-one at the 140 sampling from outlet FLASH could be concluded that the value of all parameters still below the maximum threshold. 140 FLASH have been applied and gave satisfaction result for 100 % effective meet the quality standard value in accordance with regulation of the Minister of Environment Republic of Indonesia number 5:2014 about waste water quality standards.

4. Conclusion

The FLASH treatment plant involves physical and biological pre-treatment, followed by Advanced Oxidation Processes (AOPs) based on catalytic ozonation and followed by granulated activated carbon (GAC) and powdered activated carbon (PAC) filtration. Two dominant oxidants are present in ozonation applications: ozone (O$_3$) and hydroxyl radicals (HO$_x$). Hydroxyl radicals are a highly reactive decomposition product of ozone and represent the main oxidant in AOPs. Conventional ozonation, both ozone and hydroxyl radicals can act as oxidants. In AOPs, hydroxyl radicals represent the primary transformation mechanism. In year 2015, 140 FLASH have been applied and gave satisfaction result for 100 % effective meet regulation Ministry of Environment of Republic Indonesia for waste water quality standards Number Number 5/2014. BUMA FLASH treatment is the first develop hospital wastewater treatment in Indonesia based Catalytic Ozonation Based Advanced Oxidation Process.

Acknowledgement

The authors would also like to thank to Hospital and Community Health Centre Facility in Indonesia for using outlet wastewater treatment facilities. The authors are grateful to Sucofindo, BLKPAK, SysLab, BRSI Padang, PT Mutuagung Lestari for their assistance with the analysis.

References

[1] Arslan A, Veli S and Bingöl D 2014 Sep. Purif. Technol. 132 561
[2] Lee Y, Kovalova L and Mcardell S 2014 Water Res. 64 134.
[3] Hansen K 2016 *Chem. Eng. J.* **290** 507.
[4] Zheng J 2017 *Chem. Eng. J.*
[5] Bethi B, Sonawane S, Bhanvase B and Gumfekar S 2016 *Chem. Eng. Process.*
[6] Mahmoud W, Rastogi T and Kümerer K 2017 *Curr. Opin. Green Sustain. Chem.*
[7] Méndez E 2016 *J. Environ. Sci. Heal.*
[8] Uhrbrand K, Schultz A, Koivisto A, Nielsen U and Madsen A 2017 *Water Res.* **112** 110.
[9] Carbajo J 2016 *Chem. Eng. J.* **283** 740.
[10] Verlicchi P and Zambello E 2014 *Sci. Total Environ.* **470**
[11] Serpone N, Artemev Y, Ryabchuk V and Emeline A 2017 *Curr. Opin. Green Sustain. Chem.*
[12] Fast S, Gude V, Truax D, Martin J and Magbanua B 2017 *Process.*
[13] Peres J, Ovejero J and García J 2017 *Chem. Eng. J.*
[14] Venditti S, Klepiszewski K and Christian K 2017 Lessons Learned from European Experiences and Presentation of Case Studies
[15] AndreadakisA, Maimis D, Gavalakis A, Noutsopoulos C, Kouris N and Nikitopoulos G 2010 *Int. J. Environ. Waste. Manag.* **5** 392.
[16] Rosal R, Rodríguez A, Perdigo A, Petre A and García Ia E 2009 *Chem. Eng. J.* **149** 311
[17] Matilainen A and Sillanpa M 2010 *Chemosphere* **4** 351
[18] Antoniou M, Hey G, Rodríguez S, Spioliopoulou A, Fick J and Tysklind M 2013 *Sci. Total Environ.*
[19] Hollender J, Zimmermann G, Koepke S, Krauss M, McArdell S and Ort C 2009 *Environ. Sci. Technol.* **43** 7862.
[20] Davies J and Davies D 2010 Origins and evolution of antibiotic resistance *Microbiol Mol. Biology Rev.* **74** pp 417.
[21] Auerbach E, Seyfried E and McMahon D 2007 *Water Res.* **41** 1143.
[22] Ternes T 1998 *Water Res.* **32** 3245.
[23] Ternes T, Stub J, Herrmann N, McDowell D, Ried A and Kampmann M 2003 *Water Res.* **37** 1976.
[24] Liu J, Wong H 2013 *Environ. Int.* **59** 208.
[25] Hernández-Leal L, Temmink H, Zeeman G and Buisman N 2011 *Water Res* **45** 2887.
[26] Gao P, Munir M and Xagoraraki I 2012 *Total Environ.* **4** 73.
[27] Szczepanowski R, Linke B, Krahn I, Gartemann H, Gotzkow T and Eichler W 2009 *Microbiology* **7** 2306.
[28] Acero J and Gunten U 2001 *J. Am. Water Works Assoc.* **10** 90.
[29] M. S. Elovitz M, Gunten U and Kaiser P 2000 *Ozone Sci. Eng.* **2** 123.
[30] Rice R 1996 Applications of ozone for industrial wastewater treatment - a review *Ozone Sci. Eng.* **6** pp 477.
[31] Adams C, Wang Y, Loftin K and Meyer M 2002 *J. Environ. Eng.* **3** 253.
[32] Huber M, Gabel A, Joss A, Hermann N, Laffler D and McArdell S 2005 *Environ. Sci. Technol.* **11** 4290.
[33] Okuda T, Kobayashi Y, Nagao R, Yamashita N, Tanaka H and Tanaka S 2008 *Water Sci. Technol.* **1** 65.
[34] Bin A and Sobera-Madej S 2012 *Ozone Sci. Eng.* **2** 136.
[35] Wang Y, Zhang H, Chen L, Wang S and Zhang D 2012 *Sep. Purif. Technol.* **84**
[36] Rivera-Utrilla J, Sañez-Polo M, Prados-Joya G, Ferro-García Ia A and Bautista-Toledo I 2010 *J. Hazard Mater* **174** 880.
[37] Li C, Jiang F, Sun D, Qiu B 2017 *Chem. Eng. J.* **325** 325
[38] Chen W, Li X, Pan Z, Ma S, Li L 2016 **304** 594.
[39] Sable S *Applied Catal. B, Environ.* **209** 523.
[40] Sui M, Xing L, Sheng L, Huang S and Guo H 2017 *J. Hazard. Mater.* **227** 227.
[41] Mashayekh-salehi A, Moussavi G and Yaghmaeian K 2016 *Chem. Eng. J.*
[42] Wang J and Bai Z 2016 *Chem. Eng. J.*
[43] Yaghmaeian K, Moussavi G, Mashayekh-salehi A, Mohseni-bandpei A and Satari M 2017 *Process Saf. Environ. Prot.*

[44] Gao G, Shen J, Chu W, Chen Z and Yuan L 2017 *Sep. Purif. Technol.* **173** 55–62