REMOVAL OF SULFAMETHOXAZOLE AND CEPHALEXIN FROM WATER BY CATALYTIC OZONATION PROCESS

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REMOVAL OF SULFAMETHOXAZOLE AND CEPHALEXIN FROM WATER BY CATALYTIC OZONATION PROCESS

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

OCTOBER 2011

Specially dedicated to my beloved mother and father

ACKNOWLEDGEMENT

Alhamdulillah, Praise to Allah, first, I would like to express my sincere, and deep appreciation to my supervisor, Prof. Dr Nor Aishah Saidina Amin for her advice, mentoring, guidance and support in my research. I hereby acknowledge her valuable contribution to my educational achievements and quality assurance. She always encouraged me in difficult times and helped me to surpass through challenges during three-year tenure. I hereby also acknowledge valuable support from Prof. Madya Dr. Zulkafi Buntat from Faculty of Electrical Engineering to solve my experimental issues related to ozone measurement. Finally, I would like to thank Prof. Madya Dr. Azmi Aris for his co-operation during analysis of my experimental samples.

I would like to thank all CREG members for their support and friendship over these years. In particular, to Fauzi, Maryam, Zaki, Mahdir, Linda, and Yani are greatly acknowledged for their helpful discussions and suggestions. I also acknowledge the technical support from Dr. Muhammad Khurram Zahoor from faculty of petroleum and renewable energy engineering. I wish them all the success in their future endeavors.

I would like to thank all laboratory technicians in particular Mr. Latfi, Siti Zalita and laboratory staff form FKA, for their assistance and cooperation throughout the research work to all the administration personnel in the Faculty of Chemical Engineering, Universiti Teknologi Malaysia. I would like to thank especially to Siti Zalita from Makmal Bioprocess for her support to run HPLC analysis of my samples. Her support enabled me to complete my research in time. Lastly, thanks to everyone that I have previously mentioned and to everyone who I may have unintentionally not recognized.

ABSTRACT

This study describes the removal of sulfamethoxazole and cephalexin by catalytic ozonation process in two types of reactors i) batch stirred type and ii) water circulation type. The first step was to screen a suitable catalyst during ozonation of sulfamethoxazole in a batch type reactor. It was observed that loading of Fe_2O_3/CeO_2 did not suppress the adsorption capacity of PAC and that adsorption process was by physisorption for Fe_2O_3/CeO_2 loaded PAC or PAC. Moreover, the loading of Fe_2O_3/CeO_2 synergized the effectiveness of powdered activated carbon (PAC), for removal of sulfamethoxazole during catalytic ozonation. Complete removal of sulfamethoxazole was observed using Fe_2O_3/CeO_2 loaded PAC catalyst within 5 min of ozonation on batch reactor. Further screening of catalyst suggested granular activated carbon (GAC) was a better catalyst compared to CeO_2, MnO_2, and MnO_2-CeO_2 metal oxides. In the presence of GAC as catalyst, approximately 90 % of cephalexin was removed in 5 min during batch ozonation process. GAC assisted ozonation of two antibiotics was conducted in a newly developed circulating reactors. Circulating batch reactor removed > 98 % of sulfamethoxazole and > 80% of COD using GAC as catalyst in 15 min duration. Similarly, 80-100% of cephalexin was removed using circulation batch reactor. Biodegradability was increased to more than 90% and 98% for cephalexin and sulfamethoxazole antibiotics respectively using circulating batch ozonation. Finally, a separate study was performed for solid phase regeneration of GAC to emulate the effectiveness of in-situ regeneration during ozonation process. In situ ozonation regenerated GAC efficiently. BET analysis, TPD-N_2 and TGA profiles of regenerated GAC resembled more of virgin GAC and differed from saturated GAC sample.

ABSTRAK

Kajian ini menerangkan penyingkiran sulfamethoxazole dan sefaleksin di dalam proses ozonisasi pemangkin di dalam dua jenis reaktor, iaitu (i) berkelompok teraduk dan (ii) edaran air. Langkah pertama adalah memilih mangkin yang sesuai semasa ozonisasi sulfametoksazol dalam reaktor berkelompok teraduk. Pemerhatian menunjukkan bahawa pemuatan Fe_2O_3/CeO_2 tidak menyekat keupayaan penjerapan serbuk karbon teraktivasi (PAC) dan proses penjerapan adalah berupa *physorption* untuk Fe_2O_3/CeO_2 dimuatkan PAC atau PAC sendiri. Tambahan pula, pemuatan Fe_2O_3/CeO_2 mensinergikan keberkesanan PAC, untuk penyingkiran sulfamethoxazole semasa ozonisasi sebagai pemangkin. Penyingkiran sulfamethoxazole yang lengkap telah diperhatikan apabila menggunakan mangkin Fe_2O_3/CeO_2 dimuatkan PAC dalam masa 5 minit ozonisasi pada reaktor kelompok. Pemeriksaan lanjut pemangkin mencadangkan karbon berbutiran diaktifkan (GAC) sebagai pemangkin yang lebih baik berbanding untuk CeO_2, MnO_2, dan oksida logam MnO_2-CeO_2. Dengan kehadiran GAC sebagai pemangkin, kira-kira 90% cephalexin dikeluarkan dalam 5 minit semasa proses ozonisasi kumpulan. GAC ozonisasi dibantu dua antibiotik telah dijalankan dalam reaktor berputar yang baru dibangunkan. Reaktor kelompok berputar mengeluarkan > 98% sulfamethoxazole dan > 80% COD menggunakan GAC sebagai pemangkin dalam tempoh 15 min. Begitu juga, 80-100% cephalexin telah disingkirkan menggunakan reaktor kelompok berputar. Biodegradasi telah meningkat kepada lebih daripada 90% dan 98% bagi antibiotik cephalexin dan sulfamethoxazole, masing-masing menggunakan kumpulan ozonisasi berputar. Akhir sekali, satu kajian berasingan telah dilaksanakan untuk penjanaan semula fasa pepejal GAC untuk mengikuti keberkesanan penjanaan semula in-situ semasa proses ozonisasi. Ozonisasi in-situ menjana semula GAC dengan cekap. Analisis BET, TPD-N_2 dan profil TGA untuk GAC yang dijana semula didapati menyerupai GAC asal dan berbeza dari sampel GAC tepu.

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LIST OF ABBREVIATIONS

Al_2O_3	-	Aluminum dioxide
ANOVA	-	Analysis of Variance
AOPS	-	Advanced oxidation process
BOD	-	Biological oxygen demand
CEX	-	Cephalexin
COD	-	Chemical oxygen demand
CTNs	-	Carbon nanotubes
DBPs	-	Disinfection byproducts
GAC	-	Granular activated carbon
GC-MS	-	Gas chromatography mass spectroscopy
HPLC	-	High performance liquid chromatography
MOPAC	-	Metal oxide impregnated powdered activated carbon
MPS_{BET}	-	Multipoint surface area
MPSD	-	Marquardt's percent standard deviation
MWNTs	-	Multiwal nanotubes
OH	-	Hydroxyl radicals
O_3	-	Ozone
O_2	-	Oxygen
PAC	-	Powdered activated carbon
PCAC	-	Petroleum coke based activated carbon
PhCs	-	Pharmaceutical compounds
RGAC	-	Regenerated activated carbon
RSM	-	Response surface methodology
SiO_2	-	Silicon dioxide
SGAC	-	Saturated activated carbon
SMX	-	Sulfamethoxazole
SOGs	-	Surface active group

SPE	-	Solid phase extraction
SPS_{BET}	-	Single point surface area measured at $P/P_o = 0.02535$
SSE	-	sum of error squares
SWNTs	-	Single wall nanotubes
TBAM	-	Tetrabutylammonium montmorillonite
TiO_2	-	Titanium dioxide
TOC	-	Total organic contents
VGAC	-	Virgin granular activated carbon
V_{mes}	-	Mesoporous volume
V_{micro}	-	Microporous volume
V_{Total}	-	Total volume
WWTPs	-	Wastewater treatment plant

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CHAPTER 1

INTRODUCTION

1.1 Pharmaceuticals as Water Pollutant

Advancements in personal care sector injected numerous varieties of pharmaceuticals in modern day health facilities. Although medications served as life saving drugs both for human and animals, their indirect addition to ecosystem has raised many questions to the environment protection [1]. Medicines are stable structures chemically to prolong medication time within the body, which sense non-degradability of such items [2]. Persistence of pharmaceuticals in industrial and municipal water streams is one of environmental hazards polluting ecosystem. Clotrimazole, Mefenamic, diclofenac, erythromycin, colifibric acid [3], Ibuprofen [4], sulfamethoxazole [5] are examples of pharmaceuticals frequently detected in municipal and waste water treatment plant effluents. Researchers have raised concerns about the transportation of pharmaceutically polluted water resources as drinking water supplies or long-term implications to the aquatic life. Although direct effect of pharmaceutical polluted water is less susceptible since concentration of pharmaceuticals in water, streams far lower than prescribed dosages level. Pharmaceuticals are design to interact with biological matter in living organisms and in their physico-chemical behavior. Many of the pharmaceuticals are lipophilic to ease their passage through cell membranes and are reactive to specific types of metabolic interactions only; otherwise remain persistent in the body cells. In a way these pharmaceuticals easily bioaccumulate within the body and induce the harmful effects of terrestrial or aquatic organisms. Figure 1.1 illustrates the exposure, fate, and long-term effects of medical compounds on aquatic organisms. Pharmaceuticals

undergo biodegradation into metabolites during the fate of such substances in the environment. Occurrence of pharmaceutical active compounds and metabolites in the environment depends upon their resistance to the biodegradability. However, presence of these pharmaceutically active substances in ground water, surface, or ocean water shows their persistence for longer time duration and mobile nature.

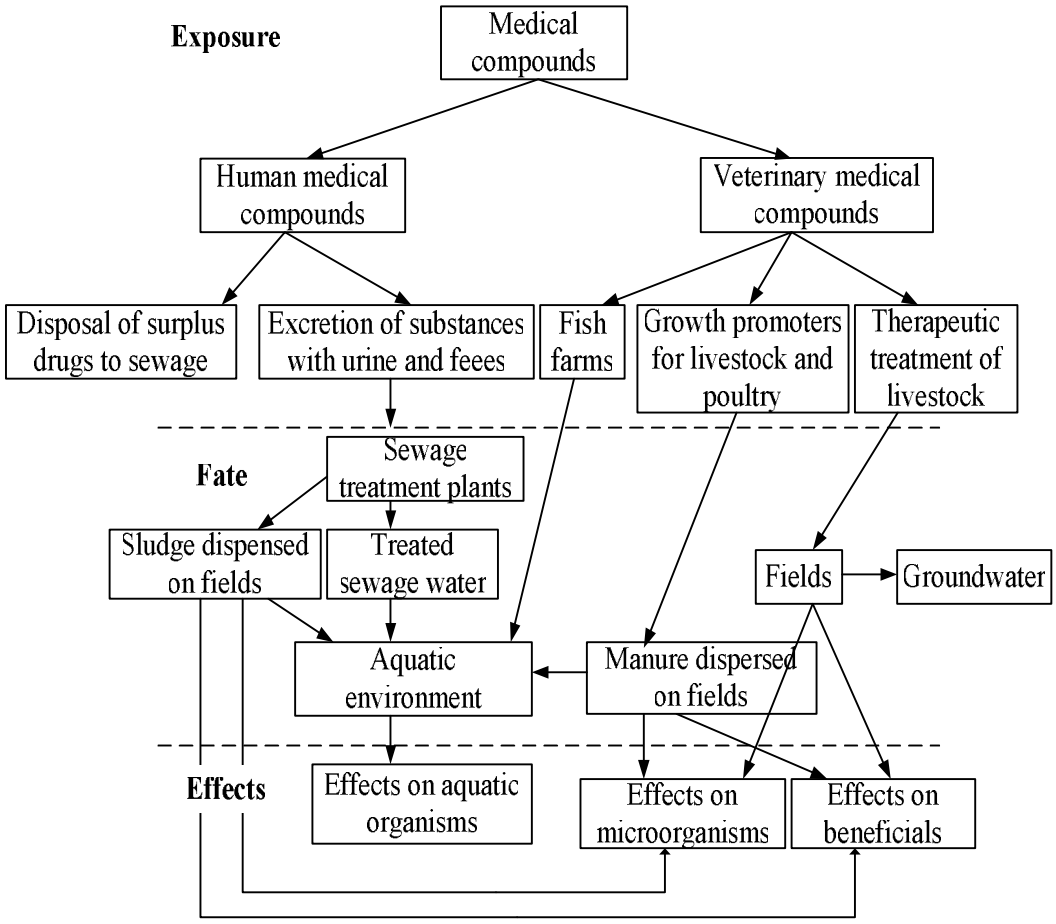

Figure 1.1 Pathways for pharmaceutical compounds in aquatic environment [6]

1.2 Removal of Pharmaceuticals at Point Source

Major sources for induction of in the aquatic environment are urban wastewater, hospitals, pharmaceutical manufacturing facilities, and treatment plants. Proper treatment of these substances at the exit of their source points may reduce the significant volume of pharmaceuticals in the aquatic environment. Treatment at the

exit point seems one viable option if we are to save our water supplies from such pollutants.

Several methods have been adopted in water treatment ranging from conventional filtration [7], biological treatments [8], coagulation [8] to activated carbon [9], electrochemical and advanced oxidation processes [10-11].These processes differ in treatment capability, operational cost, selectivity and removal efficiency. Biological methods like biofilters, activated sludge are quite effective for biodegradable pollutants. Physical techniques like adsorption, coagulations flocculation, and precipitations are suitable to remove insoluble suspended particles. Activated carbon can effectively remove dissolved organic contaminations. Reverse osmosis, micro, and nano filtrations are other methods for selective removal of micro pollutants. Other than these, advanced oxidation processes such as ozonation, UV, H_2O_2/O_3, UV/O_3, chlorination are capable of oxidizing soluble, insoluble organic and inorganic contaminants [5]. However, it is true most of the organic and inorganic toxins are removable through water treatment techniques, none of techniques is solely appropriate to handle all types of contaminations. Biological methods cannot grasp synthetic and inorganic pollutions; coagulations and flocculation are inefficient to dissolved micro pollutants; membranes are costly, chock able, and unable to treat macro pollutants; production of DBPs in advanced oxidation processes question usefulness of such operations. Presence of pharmaceuticals in wastewater treatment plants (WWTPs) effluents and water streams also confirms inefficiency of traditional techniques like coagulations, flocculation, and sedimentations [3, 5, 12]. Though it is true, the most WWTPs are equipped to handle various types of contaminations by integration of techniques in series. Bar screening, preliminary clarification, trickling filter, active sludge and UV treatment scheme is an example of such integrations applied in Howdon water treatment works [3]. It is believed that inclusion of ozonation or advanced oxidation processes within this integration may reduce soluble contaminations. Some researchers have reported removal of soluble pollutants using ozone and ozone-assisted oxidations [13-16]. Thus, advanced oxidation processes may be capable of reducing pharmaceuticals and synthetic dyes in wastewater streams.

Advanced oxidation processes (AOPs) have been employed for removing pharmaceuticals active compounds [17-19]; dyes and dyestuff [14, 20-21]; bacterial disinfection [22-23]; pesticides degradation [24-25] and soil decontaminations [26-27]. AOPs rely on production of hydroxyl radicals (OH) through chemical, photochemical and photo catalytic energy that is capable of converting organics into dehydrogenated products [28]. Conventional oxidants within AOPs category include ozone, H_2O_2, chlorine, chlorine dioxide, Hydroxyl ions [29]. These are called aqueous phase oxidants, which attach almost all types of organic and inorganic contaminations. Oxidation potential is one criterion to judge pollutants removal efficiency in such treatments like ozone OH (2.86), O (2.42), O_3 (2.07), H_2O_2 (1.78), Cl (1.36), ClO_2 (1.27). Performance of individual process is also dependent upon generation of hydroxyl ion ($OH^{\bullet}$) which is the most powerful oxidant of this group. For this reason, ozone and H_2O_2 are preferable due their ability to oxidize contaminations directly and through OH ion generation [30]. Due to this ability, ozone has emerged as one major pollutant oxidizer for microorganism's inactivation, metals and suspended solids oxidation, dyes and pigments discoloration, dissolved organic matter and humic acids oxidation, micro pollutants removal. Whilst chlorine and its derivates are enough to disinfect bacteria present in water their ability to generate lethal chlorinated organic compounds by reacting organic species has limited their role as disinfectants [31]. Electrochemical, Fenton, Photo-Fenton [32], TiO_2/UV [33] are names of AOPs oxidation processes in which induce energy is utilized to generate radicals and ions. Fenton reagents and TiO_2 mediums generate radicals by absorbing near-UV radiations within 300-400 nm range. Electrochemical oxidation involves anodic reactions at high voltage electrodes thus breaking water molecule into hydroxyl radical (OH). In literature, Pt, PbO_2, doped PbO_2, doped SnO_2 have been employed dominantly as anode. Ion generation reaction in equation 2.1 [28].

$$H_2O \rightarrow OH^{\bullet} + H^{+} + e^{-} \qquad (1.1)$$

AOPs are suitable to waste water treatments containing chemically stable, lethal, and/or non-biodegradable pollutants. AOPs have property to degrade any type of contaminations indiscriminately without producing any toxic intermediates at

room temperatures [20]. AOPs effluents are biodegradable due radical's ability to replace chlorines attached to ring structures of organic compounds. Rate constant of organic molecules destruction remains in order of 10^6-10^9 M^{-1} S^{-1}, thus minimizing process residence times [29]. AOPs have certain advantages over conventional water treatment methods. AOPs are not refractory to wide varieties of feed contaminations and disinfection byproducts are not usually produced which simplifies operations. AOPs are better than bioremediation and chemical coagulations because later produce sludge waste materials and operate selectively on specific types of pollutants. Post processing is costly in membrane processes due to choking problem while AOPs completely mineralize organic matter and avoid any further processing of organic materials. Carbon catalyst poisoning is the major drawback in activated carbon absorption whereas no such problems are associated with AOPs (Spartan water treatment). However, high capital and operating cost of AOPs is a major drawback when compared to biological treatments and chemical coagulations. Literature usually recommends integration of different oxidants for treatment process like O_3/UV, O_3/H_2O_2, Photo/Fenton, TiO_2/UV [30, 34] mainly due their inability to produce high concentrations of hydroxyl ions (OH) individually. One of the commonly used advanced oxidant (ozone) is highly energy intensive consumes high voltages in order of 4-20 kV. As ozone is degradable to simpler oxygen at room temperatures, high concentrations of ozone need continuous ozone generation. Other AOPs, Fenton/H_2O_2 systems produce considerable amounts of iron sludge wastes [35]. Electrochemical processes usually involve costly electrodes.

Irrespective of the practical limitations, advanced oxidation processes continued their penetration in water and wastewater treatments. Ozone has emerged as one of the popular oxidant in recent times [13, 15, 17, 19, 21, 36-38]. Probably this is because i) ozone is easily soluble in water (0.57 g/L 20 ^oC), ii) ozone decomposes readily into hydroxyl ion (OH), iii) oxidation potential is high (2.87 V) [38]. Major pollutants divisions which have been tested for ozone dosages are i) metals and inorganic substances removal ii) Oxidation of suspended and dissolved organic matter iii) bacterial and viral disinfection iv) Discoloration and v) detoxification of harmful chemicals [13, 39]. Camel and Bermond, [39] divided existing literature on ozonation in three dosage levels pre-oxidation, intermediate

ozonation and final disinfection. Ozone is added at pre-oxidation stage to remove colorants and odors, inorganic and suspended materials; to increase coagulations-decantation. Micro pollutants and DBPs are generally removed in second stage dosage, which also enhances biodegradability of organic matter. Final disinfection stage is capable of removing all types of microorganisms, micro pollutants and reducing DBPs [39]. Number of citations notified effects of ozonation on pharmaceuticals degradation from wastewater streams [17, 36, 40-43]. Thus, ozonation processes are widely accepted techniques in removal of micro pollutants like pharmaceuticals from water streams.

1.3 Problem of Statement

Organic compounds such as pharmaceuticals, active personal care products (PPCPs), industrial and household chemicals are potential threat to human health and aquatic ecosystem. These organic chemical collectively called mircopollutants involve endocrine disrupting effects and chronic effects on long-term exposure [44]. Some of the pharmaceuticals have shown ineffectiveness to advance treatment technologies such as membrane separation, activated carbon adsorption, ultraviolet radiations, and ozonation [45]. Pharmaceutical compounds are even more likely in effluents of conventional treatment plants. Therefore, it seems necessary to investigate on modern technologies to treat these new types of pollutants in water resources. Moreover, due to low concentration of these micropollutants, conventional treatments based on physical or biological treatments fail to eliminate these compounds from water properly. It may be helpful to investigate on modern treatment methods for treatment of micropollutants.

Ozonation is one attractive option to degrade pharmaceuticals at the exit of point source. Simple procedure can be the reaction of dissolved ozone with pharmaceutical compound. Pharmaceuticals are relatively active species due to the presence of different functional groups that are designed to interact with metabolism. Therefore, it is presumable that main pharmaceutical compound can degrade in short exposure to dissolved ozone. However, degree of mineralization might be low.

Simple ozonation also may not be effective in achieving high ozone mass transfer efficiency. Coupling of simple ozonation with a suitable adsorptive catalyst such as activated carbon might perform effective role in removing pharmaceutical compounds from water. Activated carbon acts as an adsorbent and catalyst during the process. Activated carbon can absorb sufficient amount of pharmaceuticals on its surface in origin and oxidized byproducts form due to its porous structure and non-selective nature. At the same time, activated carbon can decompose the dissolved ozone into oxidants such as OH/O radicals. Decomposition of dissolved ozone also induces the transfer of ozone mass from gas to liquid.

In general, sufficient amount of ozone pass through the reactor column in un-utilized form during ozonation process. That might be due to many reasons such as excess amount of ozone in the feed gas, incapability of system to dissolve gas phase ozone into the solution or inefficient reasons between pharmaceutical and ozone. Addition of catalyst as activated carbon may help the better utilization of input ozone gas. Various studies highlighted such an issue where outgoing gas retains sufficient quantity of ozone gas which either need to trap in solutions or to destroy [22, 29]. Extended post processing of gas adds capital and operation cost of ozonation processes besides wasting costly O_3 into atmosphere. Proper utilization of generated O_3 is challenging in ozonation processes that may be solved by utilizing proper absorber design, catalyzed ozonation, and ozone diffusers.

In this research we focused on the maximizing the ozone utilization during the ozonation process. Options that we tried include the usage of activated carbon as catalyst and adsorbent. Secondly, we proposed the circulating absorber column reactor with using venturi mixture. Two antibiotics were selected (sulfamethoxazole and cephalexin) as model compounds. These two are commonly prescribed medicines in daily healthcare activities across the world and are often detected in the urban water and in effluents of wastewater treatment plants. Secondly, these two belong to different class of antibiotics and represent major prescribed antibiotic classes. By using these two antibiotics, it is assumed, ozonation can be applied to other antibiotics or pharmaceuticals as well.

1.4 Research Objectives

Major objectives of the research are as follows

1. To study the degradation of two antibiotic compounds (sulfamethoxazole and cephalexin) during catalytic ozonation process.
2. To screen suitable catalyst for removal of antibiotics during ozonation,
3. To compare the performance of stirred batch reactor and circulating reactor for removal of two antibiotic compounds.

1.5 Scope of Research

1. Initial screening of catalyst is performed for degradation of sulfamethoxazole antibiotic. Initial screening is performed by comparing the performance of activated carbons, metal oxides and metal loaded activated carbon catalysts. The selected catalyst is investigated further to assess the effect of operating parameters and kinetics of sulfamethoxazole. Removal of cephalexin is investigated with screened catalyst only.
2. Dissolved ozone concentration is investigated to compare the ozone decomposition behavior of catalysts. Dissolved ozone concentration is measured in case of selected catalyst for both sulfamethoxazole and cephalexin. Some experiments are conducted to measure ozone utilization efficiency for both antibiotics.
3. Performance comparison of two reactors is investigated by degrading cephalexin and sulfamethoxazole antibiotics in circulating reactor and comparing the results with that of stirred batch reactor.
4. Analysis of the antibiotics is performed using high performance liquid chromatography (HPLC) to measure their concentration during experiments. Degree of mineralization is measured by TOC and COD analysis. While for cephalexin is analyzed by COD and biological oxygen demand (BOD) analysis. Secondary byproducts for two antibiotics are analyzed in gas chromatography mass spectroscopy (GC-MS).

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