REMOVAL OF SULFAMETHOXAZOLE AND CEPHALEXIN FROM WATER
BY CATALYTIC OZONATION PROCESS

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REMOVAL OF SULFAMETHOXAZOLE AND CEPHALEXIN FROM WATER
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requirements for the award of the degree of
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Specially dedicated to my beloved mother and father
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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 Fe₂O₃/CeO₂ did not suppress the adsorption capacity of PAC and that adsorption process was by physisorption for Fe₂O₃/CeO₂ loaded PAC or PAC. Moreover, the loading of Fe₂O₃/CeO₂ synergized the effectiveness of powdered activated carbon (PAC), for removal of sulfamethoxazole during catalytic ozonation. Complete removal of sulfamethoxazole was observed using Fe₂O₃/CeO₂ 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 CeO₂, MnO₂, and MnO₂-CeO₂ 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-N₂ 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 Fe₂O₃/CeO₂ tidak menyekat keupayaan penjerapan serbuk karbon teraktivasi (PAC) dan proses penjerapan adalah berupa physisorption untuk Fe₂O₃/CeO₂ dimuatkan PAC atau PAC sendiri. Tambah pula, pemuatan Fe₂O₃/CeO₂ mensinergikan keberkesanan PAC, untuk penyingkiran sulfamethoxazole semasa ozonisasi sebagai pemangkin. Penyingkiran sulfamethoxazole yang lengkap telah diperhatikan apabila menggunakan mangkin Fe₂O₃/CeO₂ 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 CeO₂, MnO₂, dan oksida logam MnO₂-CeO₂. Dengan kehadiran GAC sebagai pemangkin, kira-kira 90% cephalaxin 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% cephalaxin telah diisingkiran menggunakan reaktor kelompok berputar. Biodegradasi telah meningkat kepada lebih daripada 90% dan 98% bagi antibiotik cephalaxin 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-N₂ dan profil TGA untuk GAC yang dijana semula didapati menyerupai GAC asal dan berbeza dari sampel GAC tepu.
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<td>Al₂O₃</td>
<td>Aluminum dioxide</td>
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<td>ANOVA</td>
<td>Analysis of Variance</td>
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<td>AOPS</td>
<td>Advanced oxidation process</td>
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<td>BOD</td>
<td>Biological oxygen demand</td>
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<td>CEX</td>
<td>Cephalexin</td>
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<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
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<td>CTNs</td>
<td>Carbon nanotubes</td>
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<tr>
<td>DBPs</td>
<td>Disinfection byproducts</td>
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<tr>
<td>GAC</td>
<td>Granular activated carbon</td>
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<tr>
<td>GC-MS</td>
<td>Gas chromatography mass spectroscopy</td>
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<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
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<tr>
<td>MOPAC</td>
<td>Metal oxide impregnated powdered activated carbon</td>
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<tr>
<td>MPS_BET</td>
<td>Multipoint surface area</td>
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<tr>
<td>MPSD</td>
<td>Marquardt’s percent standard deviation</td>
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<tr>
<td>MWNTs</td>
<td>Multiwal nanotubes</td>
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<tr>
<td>OH</td>
<td>Hydroxyl radicals</td>
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<tr>
<td>O₃</td>
<td>Ozone</td>
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<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>PAC</td>
<td>Powdered activated carbon</td>
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<tr>
<td>PCAC</td>
<td>Petroleum coke based activated carbon</td>
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<td>PhCs</td>
<td>Pharmaceutical compounds</td>
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<td>RGAC</td>
<td>Regenerated activated carbon</td>
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<tr>
<td>RSM</td>
<td>Response surface methodology</td>
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<td>SiO₂</td>
<td>Silicon dioxide</td>
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<tr>
<td>SGAC</td>
<td>Saturated activated carbon</td>
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<td>SMX</td>
<td>Sulfamethoxazole</td>
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<tr>
<td>SOGs</td>
<td>Surface active group</td>
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<td>Acronym</td>
<td>Description</td>
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<td>--------------------------------------------------------------------</td>
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<tr>
<td>SPE</td>
<td>Solid phase extraction</td>
</tr>
<tr>
<td>SPS\text{BET}</td>
<td>Single point surface area measured at P/P_0 = 0.02535</td>
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<td>SSE</td>
<td>sum of error squares</td>
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<td>SWNTs</td>
<td>Single wall nanotubes</td>
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<tr>
<td>TBAM</td>
<td>Tetrabutylammonium montmorillonite</td>
</tr>
<tr>
<td>TiO\text{2}</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic contents</td>
</tr>
<tr>
<td>VGAC</td>
<td>Virgin granular activated carbon</td>
</tr>
<tr>
<td>V_{\text{mes}}</td>
<td>Mesoporous volume</td>
</tr>
<tr>
<td>V_{\text{micro}}</td>
<td>Microporous volume</td>
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<tr>
<td>V_{\text{Total}}</td>
<td>Total volume</td>
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<tr>
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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.

![Diagram of pharmaceutical pathways](image)

**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$_2$O$_2$, 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$_2$O$_2$ (1.78), Cl (1.36), ClO$_2$ (1.27). Performance of individual process is also dependent upon generation of hydroxyl ion (OH\') which is the most powerful oxidant of this group. For this reason, ozone and H$_2$O$_2$ 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].

$$H_2O \rightarrow OH^- + H^+ + e^- \quad \text{(1.1)}$$

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$_2$O$_2$, 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$_2$O$_2$ 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 °C), 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 unutilized 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\textsubscript{3} into atmosphere. Proper utilization of generated O\textsubscript{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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