In The Name of

GOD

Razi University

Faculty of Chemistry
Department of Applied Chemistry

M.Sc. Thesis

Title of the Thesis:

Performance of biological system and advanced oxidation processes (AOP) treating antibiotic production industrial wastewater

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Abstract

In this study, two advanced oxidation processes including UV/O_3/H_2O_2 and photocatalytic oxidation (TiO_2) processes for the treatment of synthetic amoxicillin wastewater (SAW) were examined. In part one (UV/O_3/H_2O_2 process), in order to investigate the effects of influential variables on the process performance, four independent factors involving two numerical factors, initial H_2O_2 concentration and initial pH, and two categorical factors, ozonation and UV irradiation, were selected. The process was modeled and analyzedusing response surface methodology (RSM). The region of exploration for the process was taken as the area enclosed by initial H_2O_2 concentration (0-20 mM) and initial pH (3-11) boundaries. For two categorical factors (ozonation and UV irradiation), the experiments were performed at two levels (with and without application of each factor). The response surface methodology (RSM) used in the present study was a general factorial design. In order to analyze the process, two dependent parameters (COD removal and BOD_5/COD ratio) as the process responses were studied. The variables had a synergistic effect on the response. Maximum COD removal efficiency was obtained at H_2O_2 concentration 20 mM at initial pH 11. As a result,O_3/ H_2O_2 system at pH=5 showed better performance in terms of BOD_5/COD ratio (0.40), although COD removal was 10% under this condition. From the HPLC chromatograms, complete degradation of amoxicillin was achieved. The photocatalytic (TiO_2) oxidation process was also analyzed and modeled with three numerical independent factors i.e. initial CODconcentration, initial pH and reaction time using RSM. The region of exploration for the process was taken as the area enclosed by initial COD concentration(400-2000 mg/l), initial pH (3-11) and reaction time (20-240 min) boundaries.The RSM used in this stage was a central composite face-centered design (CCFD). As a result, initial COD showed different impactat different pH on the COD removal efficiency. Maximum COD removal efficiency was 20% at COD_{in} of 400 mg/l and reaction time 240 min while maximum specific COD removal rate (SRR) was found to

be 860 mg $COD_{removed}$/g cat.h at reaction time of 30 min and COD_{in} 2000 mg/l. Maximum BOD_5/COD ratio was modeled about 0.44 at the conditions with COD_{in} 2000 mg/l and reaction time 30 min. The trend of changes in the ratio was match with the results obtained for COD removal efficiency. The photocatalytic process induced by O_3 and O_3/H_2O_2 showed COD removal efficiencies of 53 and 58%, respectively after 240 min. BOD_5/COD ratio was also determined to be 0.48 and 0.42, respectively for the conditions with O_3 and O_3/H_2O_2. Photocatalytic process with regularsequencesequence regeneration by aeration could achieve 38% COD removal efficiency. BOD_5/COD ratio was also improved to 0.44. Baffled activated sludge (BAS) was also examined treating SAW. Two independent variables (COD_{in} and MLVSS) were investigated and the process was modeled and analyzedusing response surface methodology (RSM). From the results, the ratio of food to microorganism (F/M) was found to be the most important factor for the process control. The F/M ratios less than 0.4 g COD_{in}/g VSS.d, COD removal efficiency was decreased. Maximum removal efficiency (89 %) was determined at MLVSS and COD_{in} of 4800 and 2000 mg/l, respectively. Kinetic coefficients (Y and K_d) was determined 0.0815 g $VSS_{produced}$/g COD_{rem} and 0.009 d^{-1}, respectively.

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Chapter 1

Introduction

1.1 . Industrial wastewaters

Industrial wastewaters have very varied compositions depending on the type of industry and materials processed. Some of these wastewaters can be organically very strong, easily biodegradable, largely inorganic, or potentially inhibitory. This means TSS, BOD_5 and COD values may be in the tens of thousands mg/l. Such wastewaters may also be associated with high concentrations of dissolved metal salts. The flow pattern of industrial wastewater streams can be very different from that of domestic sewage since the former would be influenced by the nature of the operations within a factory rather than the usual activities encountered in the domestic setting. Factories may operate five to seven days per week. A consequence of this can be the possibility of zero flow on days when a factory is not operating. Industrial wastewater scan have very different characteristics even for wastewaters from a single type of industry but from different locations. Examples of industrial wastewaters include those arising from chemical, pharmaceutical, electrochemical, electronics, petrochemical, and food processing industries. Many industrial wastewaters do contain such potentially inhibitory or toxic substances. The presence of such substances in an ecosystem may bias a population towards members of the community which are more tolerant to the substances while eliminating those which are less tolerant and resulting in a loss of biodiversity. For similar reasons, an awareness of the impact such substances have on biological systems is not only relevant in terms of protection of the environment but is of no less importance in terms of their impact on the biological systems used to treat industrial wastewaters. Table 1-1 summarizes typical characteristics of various industrial wastewaters.

Table 1-1. Typical industrial wastewater contaminants[1]

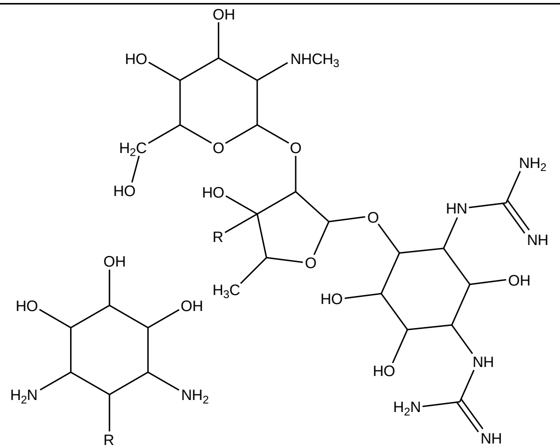
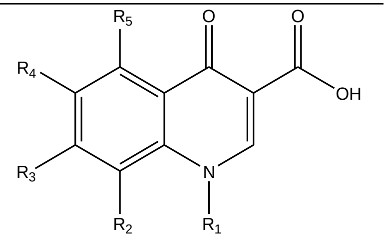
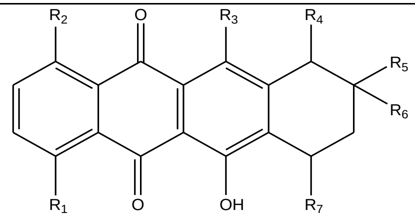
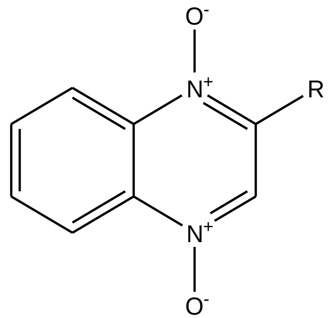
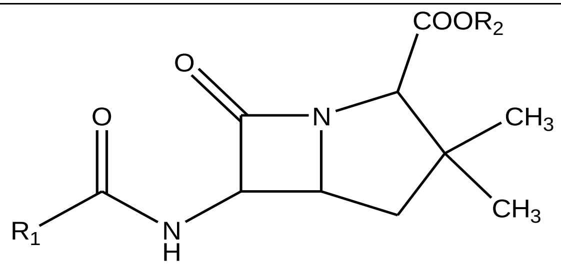
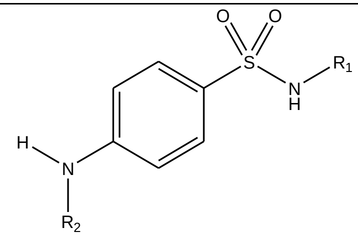
Industry	Characteristics of Wastewaters
Food Processing (dairies)	High in dissolved organics—mainly protein, fat and lactose
Meat and poultry processing	High in dissolved and suspended organics, including protein, blood, greases, fats and manure
Fruit and vegetable canneries	High in dissolved and suspended organics from natural products
Breweries and distilleries	High in dissolved and suspended organics
Pharmaceuticals	High in dissolved and suspended organics, including some surfactants and biological agent, mainly originated from mycelium, filtrate and washing processes
Organic chemicals	Dissolved organics, including acids, aldehydes, phenolics, and free and emulsified oils
Petroleum refining	Phenolics, free and emulsified oils, and other dissolved organics
Pulp and paper	Dissolved and suspended organics and inorganics
Plastics and resins	Dissolved organics, including acids, aldehydes, phenolics, cellulose, alcohols, surfactants and oils
Explosives	Organic acids and alcohols, soaps and oils
Rubber	Dissolved and suspended organics and oils
Textiles	Dissolved and suspended organics, fats and oil
Leather tanning and finishing	Dissolved and suspended organics, fats and oils, organic nitrogen, hair and fleshings
Coke and gas	High in phenolics, ammonia and dissolved organics

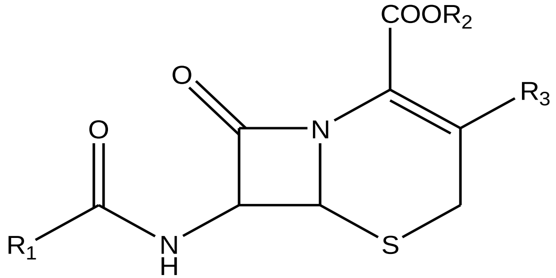
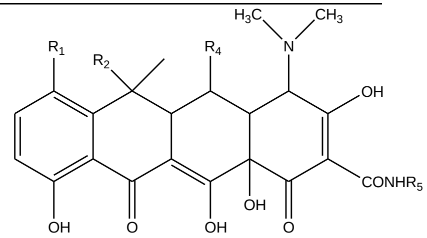
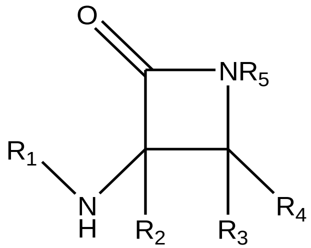
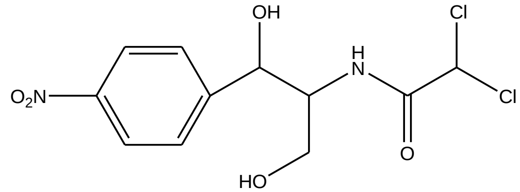
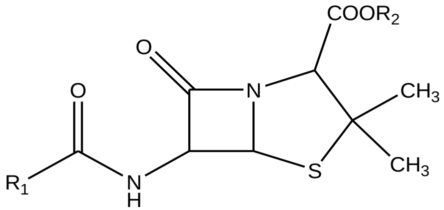
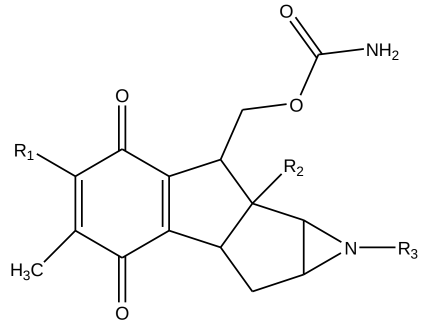
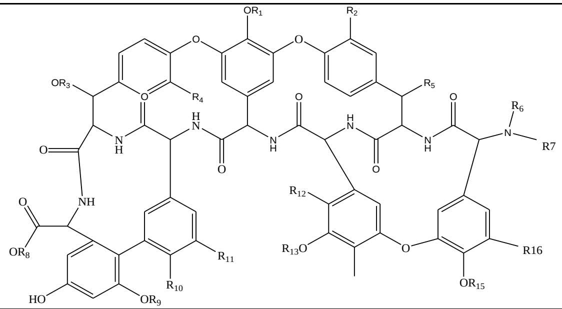
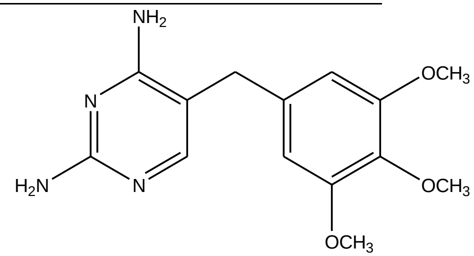
1.2 Antibiotic industrial wastewater

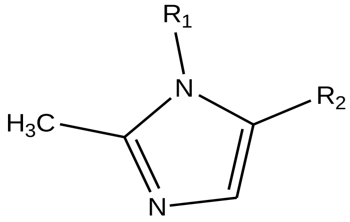
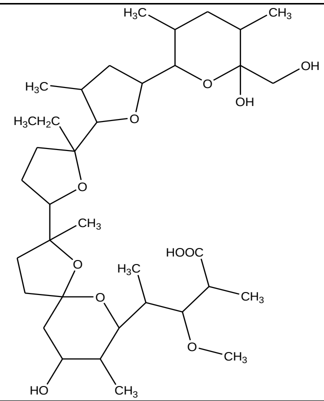
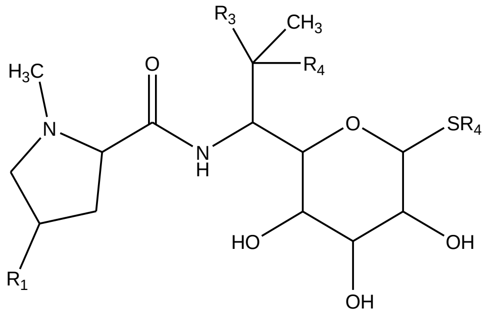
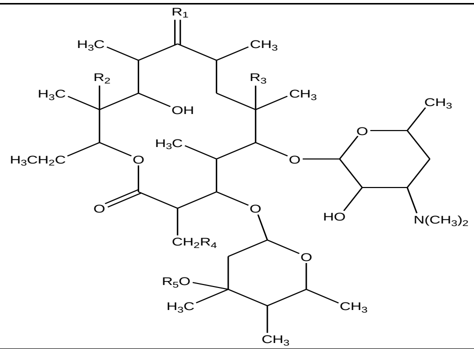
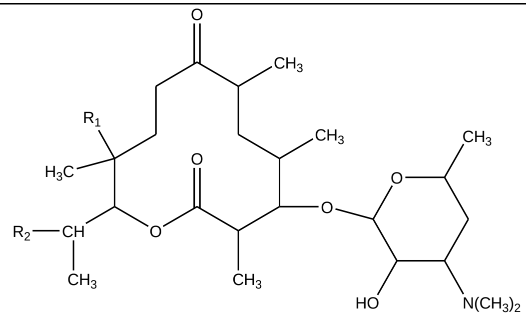
Traditionally, antibiotics are defined as chemical compounds that eradicate or inhibit the growth of other microorganism. However, the term "antibiotic" has been expanded for antibacterial, antiviral, antifungal and antitumour compounds. Most of these substances have a microbial origin, but they may be also semi-synthetic or totally synthetic. Antibiotics can be divided into several classes, according to different criteria: spectrum, mechanism of action or chemical structure. Table 1-2 presents different classes and structures of antibiotics used.

The presence of pharmaceutical compounds, namely antibiotics, in the ecosystem has been known for almost 30 years. These wastewaters contain relatively high levels of suspended solids and soluble organics, many of which are recalcitrant. Furthermore, changes in production schedules lead to significant variability of the wastewater flow rate, its principal constituents and relative biodegradability.

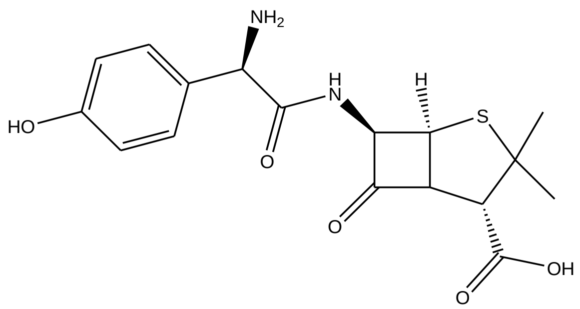
Table 1-2. Principal classes of antibiotics [2]

Class	Core structure	Class	Core structure
Aminoglycosides		Quinolones	
Anthracyclines β-Lactams		Quinoxaline derivative	
Carbapenems		Sulfonamidesz	

Cephalosporins		Tetracyclines	
Monobactams		Chloramphenicol	
Penicillins		Mitomycins	
Glycopeptides		Trimethoprim	

Imidazoles		Polyethers	
Lincosamides			
Macrolides			

These antibiotics are used as human medicine for the treatment of bacterial infections of skin, ear, respiratory tract, and urinary tract. These compounds have been widely used both for prevention and treatment of disease and as feed additives to promote growth in animal feeding operations. Amoxicillin (AMX), formerly amoxicillin in some markets, is a moderate-spectrum, bacteriolytic, β-lactam antibiotic used to treat bacterialinfections caused by susceptible microorganisms. It is usually the drug of choice within the class because it is better absorbed, following oral administration, than other β-lactam antibiotics. Molecular structure of amoxicillin is as below:



1.3 Sources of antibiotics in the environment

The sources of antibiotics in natural water systems may be manufacturing operations in pharmaceutical industry and the rapeutical use of them for human and animals. The pharmaceutical manufacturing industry produces a wide range of products to be used as human and animal medications. In these last years, the use of antibiotics in veterinary and human medicine was widespread (annual consumption of 100,000-200,000 tons) and consequently, the possibility of water contamination with such compounds increased. As mentioned above, human and veterinary antibiotics have been detected in different matrices. These pollutants are continually discharged into the natural environment as parent compounds, metabolites/degradation products or both forms by a diversity of input sources as shown in Fig. 1-1.When dispersed in the fields as fertilizer, manure can contaminate soil and consequently surface and groundwater through runoff or leaching.