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Removal of antibiotics from water and waste milk by ozonation: kinetics, byproducts, and antimicrobial activity

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ABSTRACT

The use of antibiotics in the dairy farming for curing and growth promotion results in the production of massive quantities of non-recyclable wastewater by the conventional purification techniques. Additionally, waste milk is produced during the drug withholding periods, which is not suitable for human or animal consumption and cause huge economic loss as well as present serious environmental waste. This study was designed to investigate the decomposition of various antibiotic compounds in un-buffered aqueous solutions and milk samples by ozonation process. Commonly administered broad-spectrum antibiotics such as amoxicillin, doxycycline, ciprofloxacin, and sulphadiazine were selected as model examples in the current investigation. Gradual exposure of these antibiotics to increasing ozone gas concentration induced increasing removal percentages of the antibiotics in spiked water and milk samples. The removal reached 95% across all the tested treated antibiotics with ozone dose as low as 75 $mg\,L^{-1}$. It was noted that the removal of antibiotics in milk samples is more efficient with faster rate constants. This was attributed to the self-buffering characteristic of milk that maintains the neutral pH, keeping the amine groups un-protonated and more reactive towards the electrophilic attack by the molecular ozone. ^{1}H NMR as well as HPLC experiments support the near complete removal of antibiotics and indicated the break down to simpler and more soluble fragments of acidic nature. Bacterial growth experiments, conducted with *E. coli*, and milk ageing experiments provided clear evidences that the resulting decomposition byproducts lack both toxicity effect and antimicrobial activity. This study provides a viable route to remove hazardous materials, which contribute to a growing issue of antibiotic resistance of pathogenic bacteria.

1. Introduction

In dairy farms, antibiotics are widely used to treat various diseases including bacterial infections such as Mastitis and Cystitis (Zwald et al., 2004). They are also used as growth promoters to speed the food production process and improve product quality (Dibner and Richards, 2005). Very little of the applied antibiotics is consumed while the majority is excreted without modification. This makes effluents from animal farms an important source of antibiotic in the environment. Additionally, if strict adherence to milk production withholding periods is not followed, the use of antibiotics may result residues in milk and subsequently triggers allergic reactions in humans upon consumption (Khaniki, 2007). Additionally, antibiotics give rise to an increase in the antibiotic resistance of pathogenic bacteria resulting in a long term health problems associated with the lack of availability of suitable drugs to treat the newly evolved resistant bacteria (Khachatourians, 1998; Witte, 1998). Furthermore, adherence to milk production withdrawal periods results in massive quantities of waste milk that is not suitable for human or animal (calf feeding) consumption and pose huge economic loss and present serious environmental waste (Kang'ethe et al., 2005; Selim and Cullor, 1997)

In order to prevent the problems identified above, antibiotics must be eliminated from farm wastewater as well as recycling waste milk for further use or safe environmental discharge. Several treatment processes have been proposed to remove antibiotics from aqueous media, exclusively targeting wastewater treatment plants (Homem and Santos, 2011). These processes include physical, biological, and chemical methods (Homem and Santos, 2011). The physical methods, such as filtration, coagulation, flocculation, and sedimentation have been proven to be inefficient and provide dissatisfactory results (Batt et al., 2006; Homem and Santos, 2011). They only transport the pollutants from one phase to another requiring subsequent treatments. Even advanced microfiltration coupled with reverse osmosis technology and UV radiation cannot eliminate antibiotic residues from wastewater (Batt

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et al., 2006; Gulkowska et al., 2008; Watkinson et al., 2007). Additionally, the biological method fails to remove antibiotics from wastewater due to the high toxicity and recalcitrant of antibiotics to the micro-organisms (Watkinson et al., 2007). Advanced oxidation processes (AOPs) have emerged as an important class of technologies for the oxidation and destruction of a wide range of organic pollutants in water and wastewater via the generation the strongly oxidizing hydroxyl radicals (˙OH) (Andreozzi, 1999; Stasinakis, 2008). The major drawback of AOPs is the non-readily generation of the oxidizing ˙OH radicals, requiring combinations of chemical agents, the use of toxic transition metals, or application of auxiliary energy sources such as radiation or electronic current (Badawy et al., 2006; Stasinakis, 2008; Vogna et al., 2004; Zona and Solar, 2003).

In contrast, only few attempts have been made to remove antibiotics from milk. The proposed methods include using various adsorbent materials such as activated charcoal (Charm, 1980) or functionalized resins (Geyer, 1994; Weimer, 1999) to extract antibiotics from milk. The utility of these methods are practically not feasible due to the need to heat the milk to solubilize the protein content and run it through filtration process which might not reach high separation of resins-coupled to antibiotic from the milk body. Another proposed method is using electrochemical oxidation which induces the decomposition of antibiotics present in the milk by means of oxidation (Kitazono et al., 2016). This method could be impractical solution due to its high cost and the need to add external agents such as acids and salts making the final product not suitable for recycling.

Among the different processes, ozonation, the application of molecular ozone (O_3), is a type of advanced oxidation processes (at basic pHs) that has long been used in various industries including water and wastewater treatments (Andreozzi et al., 1999). The removal of organic pollutants by this non-selective method is an oxidation based decomposition induced by the molecular ozone or the highly reactive hydroxyl radicals (˙OH), produced during the hydrolysis of ozone at basic pHs (Andreozzi et al., 1999). Ozone exhibits greater redox potential than most other traditional oxidants/disinfectants including hydrogen peroxide, permanganate, chlorine dioxide, chlorine gas, oxygen, and hypochlorite and it only competes with hydroxyl radicals and fluorine (Varga and Szigeti, 2016). Ozonation found increasing applications in the dairy industry as a disinfection agent for stainless steel surfaces used in the production factories (Guzel-Seydim et al., 2004). In fact, ozonation was used to pasteurize and preserve milk instead of the conventional thermal method without adversely impacting milk qualities (e.g., oxidizing lipids and proteins), if certain ozone levels are not exceeded (Varga and Szigeti, 2016). Additionally, ozone was used in numerous industrial areas such as food surface hygiene, recycling of wastewater, treating fruits and vegetables to increase shelf-life of the products because ozone decomposes rapidly and leaves no residues (Guzel-Seydim et al., 2004).

In this study and for the first time, we have investigated the use of ozonation treatment to remove antibiotics in raw milk and the decomposition behaviors were compared to those conducted in non-buffered aqueous solutions under the same experimental conditions. Four commonly used broad-spectrum antibiotics in veterinary medicine (Schwarz et al., 2001) (shown in Fig. 1) were selected as model examples to demonstrate the proposed method in decomposing antibiotics belonging to four different sub-classes, β-lactams, quinolone, tetracycline, and sulfonamide. The results of this study confirmed that ozonation treatment is an efficient method to remove antibiotics residues (at µM levels which commonly detected in milk samples (Aytenfsu et al., 2016; Syit, 2008)) from matrices as complex as milk with economic viability since the removal was achieved at low levels of ozone and non-agitated condition. Large-scale ozonation process is a previously proven technology in the field of water treatment (Gogate and Pandit, 2004), and can easily be transferred in recycling waste milk.

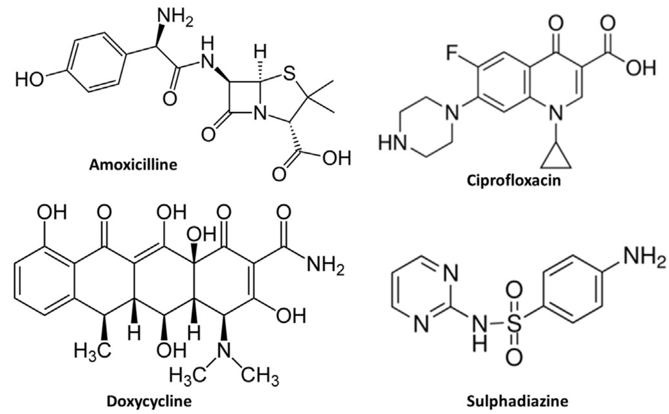

Fig. 1. Molecular structure of the studied antibiotics.

2. Experimental section

2.1. Chemicals and reagents

Amoxicillin, doxycycline, ciprofloxacin, and sulphadiazine were purchased from Alfa Aesar. Acetonitrile, *t*-butanol, and other solvents and reagents used in this study were of analytical grade and were used without further purification. Double distilled water (Mill-Q with a conductivity of 18.2 MΩ cm) was used to make stock solutions and the desired concentrations of the studied antibiotics. Milk was supplied from a local farm that is known to be free of antibiotic administration.

2.2. Ozonation experiments

Ozonation runs were conducted using Longevity Resources Inc. ozone generator model EXT50 throughout the experiments. The generator was supplied with 100% pure oxygen gas with a flow rate of 0.75 litter per minute resulting in ozone nominal yield of 7.5 $\mu g\,mL^{-1}$. All experiments were carried out in a 500 mL conical contact flask. The ozone was generated, driven by an air pump and fed into a conical flask through a pipe with a porous Teflon gas sparger located at the end of the pipe. The position of the sparger was in the middle of the test solutions. The initial antibiotics concentrations (200 µM) were made in 200 mL double distilled water and ozonated at different times (0, 2 min, 5 min, and 10 min) to produce different concentrations of ozone in the treated solutions (0, 15 $mg\,L^{-1}$, 37.5 $mg\,L^{-1}$, and 75 $mg\,L^{-1}$) or (0, 312 µM, 781 µM, and 1500 µM). Ozonation experiments of antibiotics in milk were conducted following the same procedure as above. All ozonation experiments were conducted at room temperature, 23 ^{0}C, to mimic real world application in milk samples. The degree of which the samples were exposed to ozone is discussed throughout the paper in terms of exposure time and ozone concentration exchangeably. In this study and consistent with previous reports including (Zhang et al., 2006), the ozone doses were reliably calculated from the ozone generator flow rate, ozone yield, and treatment time since the experimental conditions of the present study do not produce ozone concentration that exceeds saturation levels.

2.3. Steady state UV–VIS studies

Initially, the effect of ozone treatment on the decomposition of antibiotics (concentration of 200 µ) was studied in double distilled water (note: all studied antibiotics are water soluble at this concentration). UV–VIS spectra were recorded before and after ozonating the samples for different times (2–10 min). Unknown concentrations were determined by a comparison made against calibration curves established from at least five different standard concentrations. The spectra were collected using LAMBDA 850 UV/VIS spectrophotometer

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