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Rapid removal and photodegradation of tetracycline in water by surfactant-assisted coagulation–sedimentation method

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ABSTRACT

Surfactant-assisted coagulation–sedimentation method was applied and optimized for the effective removal of tetracycline from water. The method was conducted by adding aqueous solutions of aluminum(III) chloride, sodium dodecyl sulfate (SDS), and then sodium hydroxide to water. Tetracycline, which is hardly removed by conventional coagulation–sedimentation methods, was well collected to SDS-impregnated precipitate. Mass spectrometric and molecular probe studies indicated that the precipitate provides hydrophobic region corresponding to 1-octanol or ethyl acetate and that tetracycline was sorbed on the precipitate as the ion-pair of its aluminum chelate with a dodecyl sulfate ion. The use of 5 mg L^{-1} aluminum(III) ions and 80 mg L^{-1} SDS allowed nearly complete (>99%) removal of tetracycline in the pH region from 5 to 8.5. Continuous treatment was also achieved in a laboratory-scale experiment. Tetracycline collected to the precipitate was rapidly degraded by irradiating ultra-violet (365 nm) light. The proposed method was also useful for removing other tetracyclines as well as fluoroquinolones and different pharmaceuticals. Applicability to wastewater treatment was examined by using secondary effluents of municipal sewage treatment plants and synthesized hospital wastewaters.

Introduction

Tetracyclines are broad-spectrum antibiotics which are most commonly used in the livestock farming and often prescribed for human therapy. They are one of the most frequently detectable antibiotics in surface water resources that receive discharges from agricultural effluents and municipal wastewater treatment plants [1,2]. Their removal efficiencies are largely dependent on kinds or operating conditions of wastewater treatment and often insufficient even by full-scale wastewater treatment plants [3,4]. Tetracyclines have high risk of the occurrence of antibiotic-resistant bacteria in activated sludge, and therefore tetracycline-resistant genes have often been found at outfall of or downstream municipal wastewater treatment plants [5–7]. Therefore, efficient methods for removing tetracyclines from wastewaters have to be developed for reducing environmental risk of these antibiotics.

Several methods have been developed for the effective removal or degradation of tetracyclines in wastewaters. Ozonation is one of the most promising method for degrading tetracyclines in water [8,9]. However, their successful application seems to be limited to relatively clear drainages or secondary effluents. In the application to secondary effluents of antibiotic manufacturing wastewater, high ozone dosage is necessary for the sufficient degradation [10]. Occurrence of potentially toxic byproducts may be another environmental concern [8]. Photodegradation and photocatalytic degradation seem attractive manners for degrading photo-sensitive tetracyclines but required high electricity consumption for continuous irradiation of ultra-violet (UV) light [11–13]. Coagulation–sedimentation methods based on the coprecipitation with metal hydroxides have extensively been employed for removing dissolved organic substances [14,15] and also applied to the removal of tetracycline [16]. However, the removal ratio is not so high, probably because of the formation of the complexes with aluminum(III) or iron(III) ions that are hard to sorb on metal hydroxides [17].

Recently, we reported an efficient method for the removal of cationic dyes from water to aluminum hydroxide precipitate in the presence of an anionic surfactant, sodium dodecyl sulfate (SDS) [18]. In the proposed method, SDS molecules were incorporated into the aluminum hydroxide and formed hydrophobic precipitate. Cationic dyes in water were well sorbed on the precipitate because

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of the distribution to the hydrophobic region of the precipitate probably as their hydrophobic ion-pairs with dodecyl sulfate ion. This method (surfactant-assisted coagulation–sedimentation method) may be useful for highly efficient removal of tetracycline antibiotics from water.

In the present study, surfactant-assisted coagulation–sedimentation method was applied and optimized for the efficient removal of tetracycline (TC) from water. Experimental conditions and mechanism were investigated based on the mass spectrometric measurement of chemical species and molecular probe study of precipitate. Continuous treatment and photodegradation of concentrated TC were also studied. The removal of other tetracyclines, fluoroquinolones, and different pharmaceuticals was also examined. Applicability to wastewater treatment was investigated by using secondary effluents of municipal sewage treatment plants and synthesized hospital wastewaters.

Materials and methods

Chemicals

An Al(III) solution (1.85 M, 50 g L^{-1} as Al) was prepared by dissolving aluminum(III) chloride hexahydrate in water. Sodium dodecyl sulfate (SDS, Wako Pure Chemical, Osaka, Japan) was used as 50 g L^{-1} aqueous solution. Tetracycline antibiotics; tetracycline (TC) hydrochloride, oxytetracycline (OTC) hydrochloride, and chlortetracycline (CTC) hydrochloride, were obtained from Wako Pure Chemical. Fluoroquinolone antibiotics; norfloxacin (NOR), ciprofloxacin (CIP), levofloxacin (LEV), and enrofloxacin (ENR), as well as other drugs; chlorpheniramine maleate, diphenhydramine hydrochloride, fluoxetine hydrochloride, ibuprofen, mefenamic acid, oxybenzone, triclocarban, and triclosan were purchased from Tokyo Chemical (Tokyo, Japan). A molecular probe, *N*-phenyl-1-naphthylamine (PN, AccuStandard Inc., New Haven, CT, USA), was used as 1.0 mM ethanol solution. Water was purified with a Milli-Q Integral Water Purification System (Merck Millipore, Billerica, MA, USA) having a UV irradiation unit.

Removal of antibiotics

10-μL of Al(III) solution and 0–240 μL of SDS solution were added to 100 mL of water containing 0.1 mg L^{-1} each of antibiotics or pharmaceuticals. The solution was mixed (120 rpm) by using an AS ONE KSI-8 magnetic stirrer (Tokyo, Japan). The solution's pH was adjusted to typically 7 by adding 4 M sodium hydroxide solution with a micropipette. The resulting solution was further mixed for 15 min to ensure the coagulation of precipitate. The solution was centrifuged at 1500 rpm ($300 \times g$) for 5 min for the rapid separation of the precipitate. A 5 mL-portion of supernatant was collected to a Teflon®-capped test tube and heated at 60 °C for 30 min after adding 50 μL of 0.2 M EDTA. A 100-μL aliquot of the solution was introduced into a JASCO isocratic HPLC 2000 system (Hachioji, Japan) with an InertSustain C18 column (length: 150 mm, inner diameter: 3.0 mm, particle size: 5 μm, GL Sciences, Tokyo, Japan) for the separation and determination of antibiotics. The composition of mobile phase was 20% (v/v) (for tetracyclines) or 30% (v/v) acetonitrile (for fluoroquinolones) containing 10 mM ammonium acetate and 2 mM EDTA. The flow rate was 0.5 mL min^{-1}. The detection wavelengths were 360 nm for tetracyclines and 280 nm for fluoroquinolones.

For the application to wastewater, three secondary effluents sampled at outfalls of municipal sewage treatment plants (activated sludge) and two model wastewaters were used. The effluents were passed through an Omnipore™ hydrophilic PTFE membrane filter (pore size: 1.0 μm, Merck Millipore) to remove particulate materials. Conductivity was monitored with a Horiba ES-51 conductivity meter (Kyoto, Japan). Chemical oxygen demand (COD_{Mn}) was measured by a $KMnO_4$ titration method [19]. Tetracyclines, fluoroquinolones, or other pharmaceuticals were spiked for preparing wastewater samples.

Most experiments were performed with initial antibiotic concentration of 0.1 mg L^{-1} which is higher than the concentrations typically found in hospital wastewaters or effluents from municipal sewage plants. This concentration was selected since the primary focus of the present study was to establish clear and informative trends with eliminating analytical difficulties and minimizing experimental errors that are inevitable when working at environmentally relevant concentrations.

Mass spectrum measurement

Aqueous solutions of TC, TC and Al(III), or TC, Al(III), and SDS were prepared as described above. After adjusting pH to 7, each solution was passed through an Omnipore™ hydrophilic PTFE membrane filter (pore size: 0.45 μm) to eliminate precipitate. The filtrate was introduced into a Waters 3100 mass spectrometric detector (Milford, MA, USA) for identifying chemical species of TC. Ionization voltage for electrospray ionization was 1.5 kV, while cone voltage was 40 V for detecting TC and 60 V for TC–Al complex or its ion-pair with dodecyl sulfate ion (DS^-).

Fluorescence measurement

A 10-μL portion of PN solution was added to 10 mL of aqueous solution of aluminum hydroxide containing different amount of SDS. The resulting solution was placed into a 1-cm quartz cell for the fluorescence measurement with a PerkinElmer LS-50B luminescence spectrometer (Waltham, MA, USA). The wavelength for excitation was 340 nm which is suitable for obtaining the maximum emission intensity of PN in different solvents [20,21]. The bandwidths for the both of excitation and emission were 2 nm.

Solvent extraction

For comparing with conventional solvent extraction, TC was extracted to some organic solvents including 1-butanol, chloroform, ethyl acetate, and 1-octanol. Both of aqueous and organic phases were 10 mL in volume, saturated with each other before use, and placed into a 30-mL glass vial. The extraction was performed by mixing aqueous phase containing 0.1 mg L^{-1} of TC and organic phase for 1 h in the presence or absence of 5 mg L^{-1} Al(III) and 40 mg L^{-1} SDS. After the phase separation, TC remaining the aqueous phase was determined by above described manner.

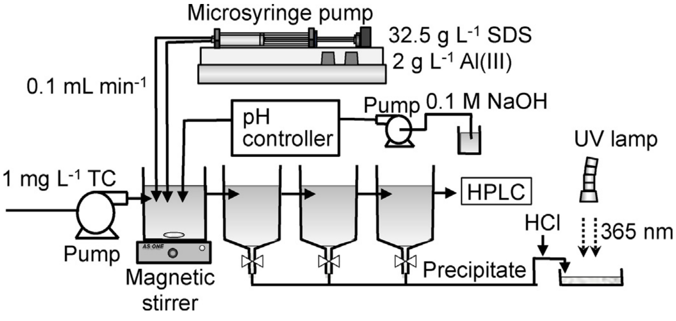

Fig. 1. Scheme of a laboratory-scale continuous treatment system.