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Removal of oxytetracycline and determining its biosorption properties on aerobic granular sludge

Hamdi Mihciokur, Merve Oguz *

Erciyes University Engineering Faculty Environmental Engineering Department, 38039, Kayseri, Turkey

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ABSTRACT

This study investigates biosorption of Oxytetracycline, a broad-spectrum antibiotic, using aerobic granular sludge as an adsorbent in aqueous solutions. A sequencing batch reactor fed by a synthetic wastewater was operated to create aerobic granular sludge. Primarily, the pore structure and surface area of granular sludge, the chemical structure and the molecular sizes of the pharmaceutical, operating conditions, such as pH, stirring rate, initial concentration of Oxytetracycline, during adsorption process was verified. Subsequently, thermodynamic and kinetic aspects of the adsorption were examined and adsorption isotherm studies were carried out. It was shown that the aerobic granular sludge was a good alternative for biosorption of this pharmaceutical. The pharmaceutical was adsorbed better at pH values of 6–8. The adsorption efficiency increased with rising ionic strength. Also, it was seen that the adsorption process was an exothermic process in terms of thermodynamics. The adsorption can be well explained by Langmuir isotherm model.

1. Introduction

Pharmaceuticals consumption has increased drastically due to technological advances in medicine and the raise in population longevity and their demands. Most pharmaceuticals are not completely metabolized by human body, and enter the ecosystems as biologically active (Boxall and Breton, 2003; Buhner, 2002). For instance, Kummerer (2001) showed that drugs used for anesthesia were excreted as 90% without metabolized (Kummerer, 2001). These drugs are usually found less biodegradable (Stuer-Lauridsen et al., 2000). Hence, these pharmaceuticals constitute bioaccumulation in aquatic environments and surroundings (Halling-Sorensen et al., 1998).

The global consumption of drugs per capita is 15 g annually with developed countries contributing three to ten times higher that value (50–150 g) (Zhang et al., 2008) So, it can be expected that the raw sewage from developed countries contains high amount of pharmaceutical compounds. Effluents from wastewater treatment plants (WWTPs) are considered significant sources of pharmaceuticals to the aquatic environment (Kimura et al., 2007) This can contribute to water pollution because of their potential toxicological impacts on aquatic organisms. Also, pharmaceuticals can return to humans via drinking water. Other exposure pathways to humans may include food chain and wastewater reuse for household purposes. The pollution of the environment by these emerging pollutants is a current topic of great concern and conventional WWTPs have a limited capability to remove these micropollutants (Halling-Sorensen et al., 1998).

Many studies have been performed in assessing environmental risks of pharmaceuticals. Whether these pharmaceuticals contribute risks to environment has been decided based on some parameters developed by EMEA (European Medicines Evaluation Authority) and EPA (Environmental Protection Agency). Among these parameters, two of them come forward for evaluating environmental risks of drugs. Those are PEC (Predicted Environmental Concentration) and PNEC (Predicted No Effect Concentration). The environmental risks of the pharmaceuticals can be classified based on their PEC and PEC/PNEC values (Halling-Sorensen et al., 1998; Jones et al., 2002; Sebastine and Wakeman, 2003).

If PEC < 0.01 μg/L, there is no need to examine the risks of pharmaceuticals. However, if 0.01 < PEC < 0.1, it should be looked into the ratio of PEC/PNEC. Similarly, if PEC/PNEC > 1, the pharmaceutical has potential environmental risks and must be investigated [8–9]. Additionally, Stockholm City Council Report, published annually, classifies pharmaceuticals based on PEC/PNEC values to evaluate their environmental risks as follows (Stockholm County Council, 2012):

If,

* Corresponding author.
E-mail address: merveoguz@erciyes.edu.tr (M. Oguz).

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PEC/PNEC < 0.1, the pharmaceutical is not significant for environment.

PEC/PNEC is between 0.1 and 1, the pharmaceutical has low impact.

PEC/PNEC is between 1 and 10, the pharmaceutical is moderately important.

PEC/PNEC > 10, the pharmaceutical has environmental risks at higher levels.

In most studies, the pharmaceutical were classified according to these parameters. For example, one study stated that some of the pharmaceuticals such as oxytetracyline, amitriptyline, thioridazine, fluoxetine and dextroproxyphene would have environmental risks in the future (Sebastine and Wakeman, 2003). This study also showed that some pharmaceuticals can discharge to water without completely metabolized and that harmful effects of these biologically active pharmaceuticals on human body were still unknown despite their low concentrations in environment (Halling-Sorensen et al., 1998; Sebastine and Wakeman, 2003).

In addition, this study specifically mentioned antibiotics stating that antibiotics not only kill harmful microorganisms but also could kill all microorganisms in aquatic environment. The pharmaceuticals studied in this research have higher PEC/PNEC values which are as following: Oxytetracyline (PEC/PNEC: 26.8), amitriptyline (PEC/PNEC: 1.29), dextropropoxyphene (PEC/PNEC: 2.06) and thioridazine (PEC/PNEC: 2.59) (Sebastine and Wakeman, 2003).

The studies investigating biodegradation of pharmaceuticals in activated sludge confirmed that most of those such as Amoxicillin, Ciprofloxacin, Oxytetracycline, Thioridazine etc. cannot be biodegraded (Halling-Sorensen et al., 1998; Jones et al., 2002; Richardson and Bowron, 1985; Kummerer et al., 1997, 2000). In addition, some research showed that especially Oxytetracycline was observed in aquatic environments; thus, the occurrence of Oxytetracycline in surface waters and in aquatic organisms has raised concern as ecotoxicological effects to aquatic organisms have been reported. For instance, concentrations of Oxytetracycline in rivers in China are measured in the range of 0.235–0.712 mg/L (Li et al., 2008). Since Oxytetracycline is a broad-spectrum antibiotic, active against a wide variety of bacteria and its incomplete elimination in WWTPs, alternative treatment methods should be investigated.

Granular sludge sequencing batch reactors (SBR) are regarded as one of the promising biotechnologies in wastewater treatment Aerobic granular sludge offers an interesting alternative for conventional activated sludge systems due to its excellent physical characteristics. Compared to conventional activated sludge processes, the aerobic granular sludge technology has several advantages such as a denser and stronger microbial aggregate structure, a higher biomass concentration, excellent settling properties, capability of simultaneous chemical oxygen demand (COD), nitrogen and phosphate removal and good biosorption properties and the ability to withstand shock loads. It is also simple and flexible in operation and cheaper (Liu et al., 2003).

The aerobic granules are formed by self-aggregation of microorganisms which perform different and specific roles in biodegradation of organics during wastewater treatment. Previous studies have already shown that aerobic granular sludge is extremely promising for the treatment of effluents containing toxic compounds (Amorim et al., 2014; Moreira et al., 2015). To date, treatment of wastewater containing pharmaceuticals has been reported using physicalechemical processes such as electrochemical oxidation and advanced oxidation processes. Biological processes using activated sludge systems have been reported but complete elimination of the pharmaceuticals has not been achieved. Up to now, there is a lack of information regarding the removal of Oxytetracycline using aerobic granular sludge technology and their effect in the nutrient removal processes in such systems.

The main objective of this study was to assess the removal of Oxytetracycline using aerobic granular sludge as an adsorbent and to evaluate its degree of attachment to the granular sludge.

2. Materials and methods

2.1. Chemicals

Oxytetracycline (>99% in purity) was purchased from Sigma-Aldrich Chemie (Steinheim, Germany). The stock solutions of Oxytetracycline were prepared daily and dilutions were performed to obtain desired concentrations. All other chemicals used in this study were of the highest purity commercially available (Sigma-Aldrich Chemie, Steinheim, Germany; Merck, Darmstadt, Germany; Carlo Erba, Val de Reuil, France).

2.2. SBR set up and formation of aerobic granular sludge

A SBR with a working volume of 3.14 L was used in this study. The column reactor had a water height of 40 cm and an internal diameter of 10 cm. Activated sludge from a municipal WWTP (2 L) was used as inoculum for the start-up of the SBR. The pH was maintained at 7.0 ± 0.8 by dosing 0.1 N H_2SO_4 or 0.1 N NaOH (Mağden Aleksanyan, 2010).

The reactor was initially operated in successive cycles of 6 h consisting of 30 min settling. After, the settling time was decreased to 2 min to retain only particles with a settling velocity larger than 6 m/h in the reactor (Mağden Aleksanyan, 2010).

Scanning electron microscope (SEM) images were taken by Erciyes University Technology Research and Implementation Center to have an idea about the bacterial population. To investigate the effects of surface area on adsorption, properties of sludge surface area were determined using a BET instrument. In addition, FT-IR spectrum analyses were performed in Bozok University Chemistry Department to decide the functional groups of the sludge, the effects of those groups on the adsorption process and whether the adsorption was physical or chemical. The spectrums were obtain in the range of 4000–400 cm^{-1} and recorded by a Perkin Elmer Spectrum 2 FTIR spectrometer & ATR instrument.

2.3. Synthetic wastewater composition

The compositions of the SBR influent wastewater and trace elements solution for 1 L were given in Table 1.

2.4. Measurement of oxytetracycline in aqueous solutions and in sludge-water mixture

Oxytetracycline concentrations were measured by a spectrophotometer based on methods used in the literature (Cazedey and Salgado, 2012; Nijhu et al., 2011; Zoltan et al., 2007; Gujral and Haque, 2010; Dikran and Hussan, 2009; Gallego and Arroyo, 2002; Prasad and Rao, 2010; Joanna Karpińska and Sokol, 2003; Didamony and Hafeez, 2012). To decide wavelengths that Oxytetracycline gives maximum absorbance, a wavelength scanning in the range of 200–400 nm, in 5 cm beam path length and 1 nm spectral band width for 2.5 mg/L Oxytetracycline using a spectrophotometer (Hach-Lange DR 5000) was performed (Fig. 1). Based on the results, the wavelengths in which the measurements of the pharmaceutical were carried out were decided.

Oxytetracycline gave two characteristic peaks at 354 nm and 266 nm which are comparable with the values in literature (Cazedey and Salgado, 2012; Nijhu et al., 2011; Zoltan et al., 2007; Gujral and Haque, 2010; Dikran and Hussan, 2009; Gallego