



Research article

Removal of Mefenamic acid from aqueous solutions by oxidative process: Optimization through experimental design and HPLC/UV analysis



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ABSTRACT

Mefenamic acid (MEF) is a non-steroidal anti-inflammatory drug indicated for relief of mild to moderate pain, and for the treatment of primary dysmenorrhea. The presence of MEF in raw and sewage waters has been detected worldwide at concentrations exceeding the predicted no-effect concentration. In this study, using *experimental designs*, different oxidative processes (H₂O₂, H₂O₂/UV, fenton and Photo-fenton) were simultaneously evaluated for MEF degradation efficiency. The influence and interaction effects of the most important variables in the oxidative process (concentration and addition mode of hydrogen peroxide, concentration and type of catalyst, pH, reaction period and presence/absence of light) were investigated. The parameters were determined based on the maximum efficiency to save time and minimize the consumption of reagents. According to the results, the photo-fenton process is the best procedure to remove the drug from water. A reaction mixture containing 1.005 mmol L⁻¹ of ferrioxalate and 17.5 mmol L⁻¹ of hydrogen peroxide, added at the initial reaction period, pH of 6.1 and 60 min of degradation indicated the most efficient degradation, promoting 95% of MEF removal. The development and validation of a rapid and efficient qualitative and quantitative HPLC/UV methodology for detecting this pollutant in aqueous solution is also reported. The method can be applied in water quality control that is generated and/or treated in municipal or industrial wastewater treatment plants.

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1. Introduction

There are numerous potentially hazardous chemicals and new substances constantly being developed and released into the environment. In recent years, research on water pollution has increasingly focused on a new group of pollutants known as emerging contaminants (Bolong et al., 2009). Pharmaceutically active substances are an important group of emerging contaminants. Their extended use and the incomplete elimination in wastewater treatment plants have resulted in these contaminants, in their native form or as metabolites, continuously introduced into sewage waters, mainly through excreta, disposal of unused or expired drugs, or directly from pharmaceutical discharges (Gros et al., 2007; Bueno et al., 2009 and Verlicchi et al., 2012). This

fact, together with the reported evidence of harmful effects produced in the natural ecosystems (Bringolf et al., 2010 and Fent et al., 2006), has recently prompted calls for some pharmaceuticals to be included in the European Union's priority list of pollutants (European Commission, 2013).

Mefenamic acid, IUPAC name 2-(2,3-dimethylphenyl)amino-benzoic acid, is a non-steroidal anti-inflammatory drug (NSAID), indicated for relief of mild to moderate pain, and for the treatment of primary dysmenorrhea (Rawlinson and Davis, 1983, Patient, 2014). The presence of mefenamic acid has been detected in sewage effluents as well as in receiving waters in different countries (Gros et al., 2007; Araujo et al., 2011; Tauxe-Wuersch et al., 2005; Jone et al., 2006 and Soulet et al., 2002). In treated effluent, mefenamic acid has been detected at concentrations exceeding the predicted no-effect concentration of 0.43 µg/L (Fent et al., 2006, Werner et al., 2005). Studies have pointed out that mefenamic acid was persistent in wastewater effluents after municipal wastewater treatment (Tauxe-Wuersch et al., 2005). The Advanced Oxidation Processes (AOP) have shown to be promising for

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degrading this pharmaceutical compound. The ozonation and O_3/UV degradation processes are the most commonly studied evaluation techniques (Gimeno et al., 2010; Gerrity and Snyder, 2011; Chang et al., 2012). The combination of ozone and UV radiation led to the best results, which exhibited MEF removal percentage of 60–80%. The use of UV/H_2O_2 , Fenton and photo-Fenton in MEF degradation is also described, focusing on the degradation of this compound in municipal wastewater treatment plant effluents and in the presence of over 31 compounds (De la Cruz et al., 2012). In this study univariate analysis were carried out evaluating the H_2O_2 and catalyst concentration parameters and in a limited range (10, 25 and 50 mg L^{-1} of H_2O_2 and 5 mg L^{-1} added or 1.48 mg L^{-1} of total iron already present). Due to the fact that an oxidative process has many potentially important variables for its effectiveness, the evaluation of all these parameters using a univariate analysis requires many experiments, and the lack of correlation between all the variables can result in inaccurate results. Optimization strategies that use chemometric tools are generally more efficient and economical than the univariate analysis, since they allow studying the interactions between two or more variables in order to assess to what degree this interaction effects all other parameters in the system (Bruns et al., 2006; Rozaca et al., 2010 and Arslan-Alaton et al., 2010). This evaluation is important to define a process that is efficient, faster, simpler and at lower cost, enabling its application in municipal water and wastewater treatment. Multivariate analysis evaluating the influence and interaction effects of the most important variables in the oxidative process not been reported yet for MEF and it was applied in this study in this context. The fractional factorial design was proposed to simultaneously evaluate the different types of AOPs, as well as the influence and interaction effects of the seven most important variables in the oxidative process. The response surface methodology was developed to establish the best concentrations of hydrogen peroxide and catalyst (ferrous ions) and to provide an optimal region for more efficient mefenamic acid degradation. The fractional factorial designs were chosen because these types of designs are widely used in experiments involving several factors. This is also usually performed early in a response surface study, since it allows to identify, with a limited number of experiments, which factors have a significant effect and which can be considered as having little or no effect on the response (Montgomery, 1984; Torrades et al., 2003; San Miguel et al., 2014 and Zakrzewska et al., 2014).

2. Experimental

2.1. Chemicals

Mefenamic acid (analytical standard; $\geq 99\%$ pure) was obtained from Sigma–Aldrich (St. Louis, MO, USA; product number 31058), while a generic medicament (Ponstan[®]; Medley, São Paulo, SP, Brazil) containing 500 mg of mefenamic acid was purchased from a local drug store. Purified water (resistivity 18.2 M Ω) was prepared using a Millipore (Eschborn, Germany) Milli-Q water purification system. All other reagents were of analytical grade unless otherwise stated. Methanol, acetonitrile and sulphuric acid were obtained from Mallinckrodt (Xalostoc, Edomex., Mexico), formic acid (reagent grade), sodium sulphite was from Merck (Darmstadt, Germany), sodium oxalate and a 30% (w/w) solution of hydrogen peroxide (reagent grade) were from Ecibra (São Paulo, SP, Brazil), ferric nitrate nonahydrate was from Químis (Diadema, SP, Brazil), and ferrous sulphate heptahydrate was from Synth (Diadema, SP, Brazil). Purified water (resistivity 18.2 M Ω cm) was prepared using a Millipore (Eschborn, Germany) Milli-Q water purification system.

2.2. Experimental procedures

All experiments were carried out using a recirculation flow-through UV photoreactor (Fig. 1), coupled to a thermostatically controlled bath (Nova Ética, São Paulo, SP, Brazil) and irradiated using a Philips (Amsterdam, The Netherlands) 15 W UVC lamp (λ max 254 nm; maximum incident photon flux $3.33 \cdot 10^{-13}$ photons. s^{-1}). In each experiment, the reactor was filled with 2 L of solution containing 10 mg L^{-1} mefenamic acid (prepared using the generic medicament) and operated at a flow rate of 150 $L h^{-1}$ [determined using a rotameter model AP300SS from Applitech (São Paulo, SP, Brazil)].

2.3. Hydrolysis and photolysis assay

Based on the literature data which reports that mefenamic acid is photodegraded when exposed to natural sunlight for long periods of time (Werner et al., 2005), preliminary experiments were performed in order to establish the influence of hydrolysis and photolysis process on the degradation of mefenamic acid. Hydrolysis was performed in the absence of hydrogen peroxide, ferrous ions and light and at original pH of reaction mixture (pH 6.1). Photolysis experiments were performed in the absence of hydrogen peroxide and ferrous ions, irradiating the reaction mixture, at its original pH of 6.1, with UV light (λ max 254 nm).

The kinetics of both the hydrolytic and photolytic reactions were performed determining the amounts of mefenamic acid that remained in aliquots of the reaction mixture, which were collected at adequate reaction times with a reaction of 180 min and analyzed by HPLC.

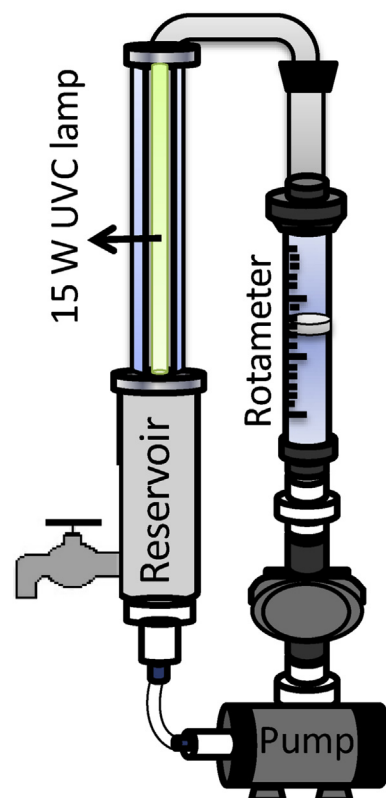


Fig. 1. Scheme of recirculation flow-through UV photoreactor.

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