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Removal of pharmaceuticals from WWTP effluent: Removal of EfOM followed by advanced oxidation

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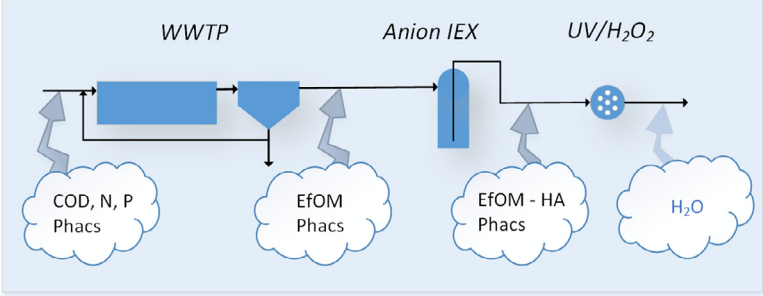
HIGHLIGHTS

- WWTP effluent contains up to 20 mg/L dissolved non-biodegradable organic matter.
- IEX can remove the humic acid fraction of effluent organic matter.
- IEX + UV/H_2O_2 is robust process for pharmaceuticals removal from effluent.
- After IEX, UV/H_2O_2 can be operated at a low dose of 300 mJ/cm^2.
- The energy demand of the UV/H_2O_2 process decreases by 84% after IEX.

GRAPHICAL ABSTRACT



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ABSTRACT

Wastewater treatment plants (WWTPs) throughout the Netherlands contain significant concentrations of pharmaceuticals (25–65 μg/L) and about 10–20 mg C/L dissolved non-biodegradable organic matter. By means of IEX mainly the humic acid fraction of the effluent organic matter can be removed, whereas O_3/biofiltration mainly removes the hydrophobic fraction. For the first time the combination of these processes with O_3/H_2O_2, UV/H_2O_2 or UV/O_3 was tested for the removal of pharmaceuticals from wastewater effluent. Based on initial laboratory experiments, a pilot installation was built in which IEX followed by UV/H_2O_2 was applied to real WWTP effluent. The process appeared to be very robust, and able to remove a very broad range of different pharmaceuticals. The additional costs for this treatment are estimated at approximately €0.34/m^3-treated effluent, which is in the same order of magnitude as estimated for other additional, but less versatile, treatment processes.

1. Introduction

Surface waters often contain a broad variety of organic micropollutants, like pesticides, industrial compounds, personal care products, steroid hormones, drugs of abuse and pharmaceuticals [1]. Increasing attention is being paid to pharmaceuticals, as these compounds have been produced to affect living organisms at low concentrations. Many pharmaceuticals are very well soluble in water, partly because that makes it easier to administer them, partly also because the European REACH regulation stimulates the use of polar compounds [2]. Besides, little is known on the effect of long term exposure and of the presence of mixtures of pharmaceuticals. Their toxicity towards certain aquatic organisms, however, has clearly been demonstrated [3–5]. It is expected that the number and amounts of pharmaceuticals used will increase significantly in the coming years, due to demographic changes and climate change [6]. The major part of these compounds and

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their metabolites appear to leave the body via urine and feces, and thus will end up in municipal wastewater. However, wastewater treatment plants in general are designed to remove COD, nitrogen and phosphorous. On average WWTPs remove about 60–70% of the pharmaceuticals, but the removal of individual compounds can vary between 0 and 100%. The remaining pharmaceuticals end up in surface waters, where they can adversely affect the aquatic environment and may cause problems for drinking water production. In the river Meuse, it was found that the summed concentrations of a series of pharmaceuticals and their transformation products range from 4 to 38 μg/L [7]. From this study, it was concluded that 90% of the total pharmaceuticals load was determined by approximately 10 compounds and the other 10% comprised over 30 chemicals. Pharmaceuticals are not regulated at the moment in the EU, but the 2013 amendment of the Environmental Quality Standards Directive (2008/105/EC) contains a mechanism to collect high-quality data on concentration of compounds of environmental concern, the so-called Watchlist. This list includes diclofenac, 17-Beta-estradiol (E2), and 17-Alpha-ethinylestradiol (EE2). For compounds on this list it is likely that regulations will be developed in future. This would mean that additional treatment of wastewater will be necessary to comply with these regulations. The Dutch Water Boards want to be prepared for this situation. Therefore, an increasing number of research projects is being done into additional treatment steps for municipal wastewater. Examples are the use of activated carbon and of ozone [8–10]. Activated carbon is less effective for the adsorption of very hydrophilic, water soluble compounds [11], especially in case competition with more hydrophobic compounds like effluent organic matter occurs. In the Netherlands the use of ozone for drinking water treatment is limited because of the relatively high bromide concentrations in Dutch surface waters, as bromide is easily converted into the known carcinogenic bromate [12]. Besides, ozone preferably reacts with electron rich molecules, so not all pharmaceuticals thus can be degraded.

For drinking water production, advanced oxidation processes, e.g. based on UV/H_2O_2, have been proven to be very successful in dealing with a broad range of organic micropollutants [13–15]. However, WWTP effluent contains much more organic matter than drinking water. This organic material competes with the micropollutants in oxidation processes, as a result of which these processes will become less effective for removing micropollutants [1,16]. Besides, in UV/H_2O_2 processes a high UV dose is required, typically around 500 mJ/cm^2, whereas for disinfection in general 20–70 mJ/cm^2 is sufficient. Because of the low UV transmittance of the effluent, the energy demand to reach such high doses will be very high. Therefore, it was studied whether the process can be optimized by removal of (part of) the Effluent Organic Material (EfOM) prior to the application of AOP. And although the EfOM removal processes and AOP are not novel techniques, it is for the first time that this combination is tested on treated wastewater effluent.

First, the EfOM was characterized and concentrations of a broad range of pharmaceuticals in Dutch WWTP effluents throughout the country were studied. Characterization of EfOM can be done in various ways. In principle EfOM consists of soluble non-biodegradable organic matter. A common method to characterize organic material is by means of LC-OCD techniques, which can (semi-) quantitatively determine the following fractions [17,18]:

- Biopolymers (BP) with molecular weight (MW) $\gg$ 20.000.
- Humic substances (HS) with MW $\approx$ 1000.
- "Building blocks" (BB) with MW $\approx$ 300–500 (These are natural conversion products of humic substances).
- Neutral components with MW < 350 (LMWn).
- Acidic components (LMW-acids) with MW < 350 (LMWa).
- Hydrophobic organic compounds (HOC) (=DOC-BP-HS-BB-LMWn-LMWa).

According to Shon et al. EfOM contains 50% proteins, 40% carbohydrates, 10% fats and oils, and traces ($\leq$μg/L) of organic micropollutants [19]. In the present research, the LC-OCD method was applied. Additionally, the occurrence of a broad range of pharmaceuticals in the wastewater was determined.

Subsequently, in one particular wastewater two different techniques were applied to remove part of the EfOM: anion exchange (IEX), and ozone followed by biofiltration. It was decided to apply IEX as a pretreatment, and the effect of this pretreatment on a subsequent UV/H_2O_2 advanced oxidation process was studied both on laboratory and pilot scale. Although in principle advanced oxidation can result in total mineralization of the organic compounds, in most cases the degradation will occur to a lesser extent. In general, it is assumed that these (smaller) molecules will be better biodegradable [16]. However, it cannot be excluded that transformation products will be formed that might be even more toxic and/or persistent than their parent compounds [1], and thus should be taken into consideration too. To obtain information on this, the fate of some known metabolites during the treatment was studied too.

2. Materials and methods

2.1. Samples from WWTP effluents

Effluent samples were taken at various WWTPs throughout the Netherlands (Fig. 1). The samples were collected with an automatic sample collector over 24 h and proportional to the effluent flow rate, after several days of dry weather.

TOC (Total Organic Carbon), DOC (Dissolved Organic Carbon) and UV-T (UV transmission at 254 nm) were measured at the KWR laboratory, and concentrations of a broad range of pharmaceuticals and some metabolites were measured according to the UPLC-MS/MS method described previously [13,20]. The composition of the EfOM was determined by DOC-Labor Dr. Huber

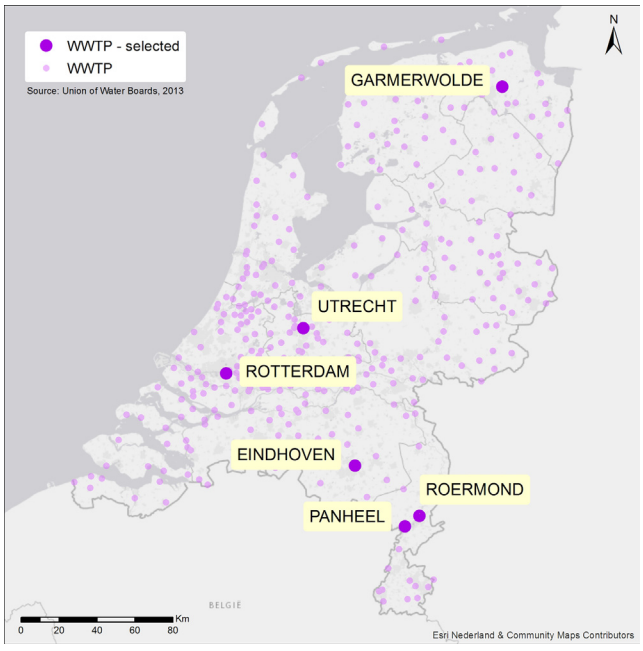

Fig. 1. WWTPs studied.