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Ozonation efficiency in removing organic micro pollutants from wastewater with respect to hydraulic loading rates and different wastewaters

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HIGHLIGHTS

- Hydraulic loading to the WWTP has little effect on the efficiency of ozonation.
- Differences in ozonation efficiency for different wastewaters cannot be linked to pH or nitrite.
- A Z-value of 0.8 mg O_3/mg TOC is a good starting point but no guarantee for good removal.

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ABSTRACT

Organic micro pollutants can be removed from water by ozonation. In this article we studied the performance of ozonation under real life conditions and compared results of the same ozonation pilot plant installed at different wastewater treatment plants (WWTPs) thus operating with different waters.

The comparability of the removal and reaction rate constants from one waste water treatment plant were low in respect to reaction rate, removal as well as to response to the specific ozone dose. Neither pH-value nor residual nitrite concentrations were the driving force considering these differences.

Further tests with different loadings were conducted at the same WWTP under different weather conditions. For the different hydraulic loading of the biological plant, the ozonation was running with rather similar removal rates concerning the same specific (TOC normalized) ozone dose. The compounds that were removed quantitatively under dry weather were still removed well with three times dry weather flow.

Using a dataset from one WWTP to optimize operation in another one is thus questionable.

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1. Introduction

The release of organic micro pollutants (OMPs) such as pharmaceuticals, personal care products, endocrine disrupting compounds and biocides to the environment with wastewater treatment plant (WWTP) effluents has gained considerable research interest in the last decades [1]. These effluents are considered to be a major source of OMPs reaching the aquatic environment [2,3] where they may have adverse effects. Cases of chronic toxicity, endocrine disruption and human health problems [4–6] have been reported.

The classical activated sludge wastewater treatment results in high removal rates for many easily degradable OMPs such as the pharmaceuticals ibuprofen and paracetamol [7,8]. On the other hand many other compounds are not removed through biodegradation or adsorption to the sludge [6]. Additional treatment steps are required to remove those compounds. Oxidation by ozone has shown to be effective in lowering the release of OMPs to the receiving waters [9–12]. Ozonation of effluent waters has been reported to result in removal of up to 95% of OMP [13]. Several studies showed that ozonation is a feasible and economical treatment [2] to improve the quality of the WWTP effluent [12–17].

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Ozone itself is a selective oxidant targeting double bonds and compounds with electron rich sites like amines and activated aromatic rings [2,17]. Ozonation in aqueous solutions results additionally in ozone decomposition and formation of hydroxyl radicals which are highly reactive and less-selective oxidants [17]. The removal efficiency is influenced by wastewater composition and properties like dissolved organic carbon (DOC) concentration and type (aromaticity, unsaturation, etc.) as well as other matrix effects [12,18–20]. The relation between the DOC and the ozone dose has been thoroughly studied and is expressed in the specific ozone dose (Z) mg O_3/mg DOC. The type of DOC can exert different ozone demands depending on the amount of unsaturation and aromaticity.

1.1. Competition of organic micro pollutant removal with DOC

In chemical oxidation processes involving ozone, the desired reaction between ozone and the target OMP is competing with reactions with other non-target compounds (expressed as DOC) present in the wastewater until all molecules with electron-rich sites are oxidized. For the other oxidation route via the less-selective hydroxyl radical, the competition from DOC is continuous during the whole process time [12]. The removal efficiency of targeted OMP using ozone is also affected by several factors such as the pH [21] as well as by the presence of hydroxyl radical scavengers. The influence of DOC on the efficiency of ozonation is usually expressed practically as (Z) mg O_3/mg DOC.

1.2. Influence of pH on removal of organic micro pollutants

1.2.1. Ozone dissociation

Several studies have shown that the removal of pharmaceuticals by ozonation of wastewater is pH dependent [14,21,22]: The ozone decomposes in aqueous solutions according to Eqs. (1)–(3). The dissociation is triggered by electron transfer reaction with electron rich aromatic molecules, e.g., in the DOC (Eq. (1)) [23,24]. The reaction continues and gives a hydroxyl radical and a hydroxyl anion (Eqs. (2) and (3)) [25]. The pH is affecting the concentration of hydroxyl anions and thus the decomposition rate of ozone and ozone life time in water [21] and consequently the amount of hydroxyl radicals produced.

$$DOC + O_3 \rightarrow DOC^{\cdot+} + O_3^{\cdot-} \quad (1)$$

$$O_3^{\cdot-} \leftrightarrow O_2 + O^{\cdot-} \quad (2)$$

$$O^{\cdot-} + H_2O \leftrightarrow {}^{\cdot}OH + OH^- \quad (3)$$

Consequently, at higher pH the ozone dissociates faster and has a shorter life time, while the amount of hydroxyl radicals generated is higher. This leads to an oxidation process dominated by the reaction with the less selective hydroxyl radicals, i.e. competition from the DOC during the whole oxidation time is getting more important at high pH values [12]. On the other hand, at lower pH the ozone is more stable, the dissociation is slower and less hydroxyl radicals is generated which leads to an oxidation process dominated by direct reaction with ozone i.e. shorter competition time from molecules with electron rich moieties in the DOC [12].

1.2.2. Dissociation of compounds

At compound level there are differences between different substances and their reactivity towards reaction with ozone or hydroxyl radicals. The dominating oxidation route, which is depending on the pH, will affect their removal efficiency, i.e. different compounds will respond differently to the change in pH. At molecular level, some molecules have multiple reaction sites such as the beta blockers metoprolol and atenolol. They have both amine groups and aromatic rings as ozone reactive sites. Protonation of the amine group blocks this site for reactions with ozone. Protonation of the amine depends on the pK_a of the amine group (metoprolol pK_a = 9.7, atenolol pK_a = 9.6) and the pH of the waste water. The reaction rate constants at the different active sites are different so the whole reactivity of the molecule is dependent on the pH [17].

1.3. Influence of nitrite on ozonation of organic micro pollutants

The nitrite ion reacts with ozone rapidly and stoichiometrically according to Eq. (4). It can exert significant ozone demand especially at low ozone doses [26]. The main product is nitrate and the produced oxygen is in a singlet state [27]. The reaction constant is in the range of 10^5 M^{-1} s^{-1} [28].

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \quad (4)$$

This ozone demand and the fast kinetics will affect the removal efficiency of the target OMPs. Several reports investigated the prediction of the removal efficiency and its relation to the water quality parameters as well as kinetics [15,26,29]. In these studies it was shown that removal rates can be predicted depending on the exposure to ozone and hydroxyl radicals and the reaction kinetics of the target OMP with ozone and hydroxyl radical. However, there were some deviations, which means that there might be some other hidden factors affecting the removal efficiency. In addition, these studies were done in lab scale as a well-controlled experiments, which is not achievable in full scale.

1.4. Potential effects on ozonation efficiency by storm events

During storm events a large amount of rain water dilute the waste water, i.e. DOC in the incoming water at the WWTP will decrease. On the other hand will shear forces in the sewer systems mobilize sewer sediments and give rise to "first flush" resulting in increased DOC. Additionally particles from the streets and other urban areas are washed into the sewer systems. The run-off water during rain events contains contaminants from the buildings and streets which usually not exist in domestic waste water [30]. Thus during storm events, the loading of the treatment plant concerning hydraulics, DOC and suspended solids (SS) as well as the loading of OMPs will drastically change and eventually give different effluent water qualities as feed for the ozonation.

1.5. Aims of the study

The aims of the study were:

A) To investigate the effects of hydraulic loading to the treatment plant on the ozonation efficiency of the treatment plant effluents.
B) To compare the ozonation efficiency for effluent waters from different WWTPs to assess if it possible to generalize different parameters from WWTP to another.

Effluent water from 10 different WWTPs were tested and 43 targeted OMPs (pharmaceuticals and biocides) were analyzed. To the best of our knowledge this is the first study with the purpose of studying comparability of ozonation efficiency in pilot plant scale which means that the tests were done in more realistic conditions while the previous studies were performed in lab scale at a well controlled systems which is somehow far from reality considering the complexity of the system.

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