Removal of pharmaceuticals in WWTP effluents by ozone and hydrogen peroxide

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ABSTRACT

Ozonation to achieve removal of pharmaceuticals from wastewater effluents, with pH values in the upper and lower regions of the typical range for Swedish wastewater, was investigated. The main aim was to study the effects of varying pH values (6.0 and 8.0), and if small additions of H_2O_2 prior to ozone treatment could improve the removal and lower the reaction time. The effluents studied differed in their chemical characteristics, particularly in terms of alkalinity (65.3–427 mg·ℓ$^{-1}$ HCO_3^-), COD (18.2–41.8 mg·ℓ$^{-1}$), DOC (6.9–12.5 mg·ℓ$^{-1}$), ammonium content (0.02–3.6 mg·ℓ$^{-1}$) and specific UV absorbance (1.78–2.76 ℓ·mg^{-1}·m^{-1}). As expected, lower ozone decomposition rates were observed in the effluents at pH 6.0 compared to pH 8.0. When pH 8.0 effluents were ozonated, a higher degree of pharmaceutical removal occurred in the effluent with low specific UV absorbance. For pH 6.0 effluents, the removal of pharmaceuticals was most efficient in the effluent with the lowest organic content. The addition of H_2O_2 had no significant effect on the quantitative removal of pharmaceuticals but enhanced the ozone decomposition rate. Thus, H_2O_2 addition increased the reaction rate. In practice, this will mean that the reactor volume needed for the ozonation of wastewater effluents can be reduced.

Keywords: ozone; pharmaceuticals; hydrogen peroxide; wastewater effluents

INTRODUCTION

A number of pharmaceuticals of differing therapeutic class, along with their metabolites, have been detected in aquatic environments (Ternes, 1998; Kolpin et al., 2002; Fent et al., 2006; Batt et al., 2006; Snyder, 2008; Verlicchi et al., 2012). The major source of these pharmaceuticals is considered to be the discharge of effluents by wastewater treatment plants (WWTPs) that are not designed for removing trace organic pollutants, in view of the recalcitrance of such pollutants to biodegradation and their limited biological activity, especially in cold climates. Accordingly, additional treatment following biological treatment is called for.

Ozonation is one of the most promising technologies for the removal of organic micropollutants contained in wastewater. The efficiency of ozone in removing pharmaceuticals and personal care products, both from water generally and from wastewater, has been tested in both laboratory- and pilot-scale experiments (Ternes et al., 2003; Huber et al., 2005; Buffle et al., 2006a,b; Bahr et al., 2007; Benner and Ternes, 2009; Hollender et al., 2009; Hansen et al., 2010; Zimmermann et al., 2011). Ozone-based oxidation can be more energy-efficient than UV-based oxidation, especially when used for treatment of waters high in UV absorbance (Rosenfeldt et al., 2006; Hansen and Andersen, 2012).

One of the benefits of using ozonation in aqueous solutions is that the hydroxyl (OH) radicals that are produced will react non-selectively with pharmaceuticals, which could be an advantage for those pharmaceuticals that are difficult to degrade by direct reaction with ozone (Lee and Von Gunten, 2010). The OH radicals are generated through the self-decomposition of ozone in water at pH levels above 7, where the hydroxide ions are acting as initiators (Hoigne and Bader, 1983). Laboratory experiments have shown that the addition of hydrogen peroxide (H_2O_2) enhances the decomposition of ozone, promoting the production of OH radicals (Von Gunten, 2003). Furthermore, non-selective oxidation by highly reactive radicals usually enhances the reaction rates of ozone-resistant compounds, which will reduce the treatment time required (Zwiener and Frimmel, 2000; Huber et al., 2003). Balcioglu and Ötker (2003) reported that adding H_2O_2 enhances both the UV absorbance (at 254 nm) removal and the decrease of COD in wastewater. The rapid reaction of OH radicals is preferable in practice since it reduces the reactor size needed for such treatment. The efficiency of ozone treatment for the removal of pharmaceuticals can also depend upon the reactivity of the wastewater matrix in general (Nöthe et al., 2009).

The present study aimed at investigating the impact of varying pH levels, within the natural interval in Sweden (pH 6–8), on the removal of pharmaceuticals from wastewater effluents by the addition of ozone. It also determined if the reactivity of ozone can be promoted by addition of small amounts of H_2O_2 at low pH levels. Since the addition of H_2O_2 can be expected to enhance the decomposition of ozone to OH radicals, it is of interest to investigate the effect this has in the case of effluents with a pH below 7, where the reaction rate can be expected to be lower and the pharmaceutical removal rate lower due to the lack of hydroxide ions that promote the decomposition of ozone.

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