Degradation Characteristics of 17 β -Estradiol by Ozone Treatment with Activated Carbon

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Abstract: The present study investigates (1) ozone treatment, (2) adsorption treatment using activated carbon treatment, and (3) ozone treatment with activated carbon for their efficacy in removing 17 β -estradiol (E2) present in an aqueous solution. Both ozone and activated carbon treatments for 20 min were effective in removing E2 (initial concentration, 100 mg/L). However, both treatments have been used for two processes, and the disposal time with these treatments is more than that of another treatment. In this study, ozone treatment with activated carbon was investigated with regard to the percentage of E2 removal, pH, and chemical oxygen demand (COD). The physical and chemical characteristics of the activated carbon surface were modified due to the ozone treatment: the surface was oxidized by ozone. The surface of activated carbon exhibited polarity groups and became porous after ozone treatment. The amount of E2 adsorbed onto the ozone-treated activated carbon surface was similar to that adsorbed onto the untreated activated carbon surface. The percentage of E2 removal by ozone treatment with activated carbon was greater than that by ozone treatment alone. Moreover, the rate of E2 removal by ozone treatment with activated carbon was higher than that by ozone or activated carbon treatments alone. Ozone with activated carbon treatment may be used for the removal of E2. However, this ozone treatment for the degradation of E2 may have a greater COD than that in the case of activated carbon treatment alone.

Key words: 17 β -estradiol, ozone, activated carbon, degradation, COD

1 INTRODUCTION

In England, feminization of fish was observed in rivers into which sewage treatment plants drained in the 1980s. This observation attracted attention to behaviors of chemical compounds in sewage possessing especially estrogen-like actions. At the beginning, the derangement of the water ecologic system caused by sewage treatment was considered to be caused by synthetic chemicals like nonylphenol. Recently, however, it was clarified that natural estrogens including 17 β -estradiol (E2), estrone, and estriol from human or livestock excreta and synthetic estrogens as well like 17 α -ethynylestradiol were major responsible agents¹⁾.

Steroid hormones are synthesized in the human body at 25-100 mg/day in adult women, more in pregnant women, and 1-25 mg/day in men as well. These hormones are inactivated by drug-metabolizing enzymes in the liver. These metabolites are further transformed in the liver or in the small intestine to sulfate conjugates or glucuronic acid

conjugates to be excreted in excreta. The conjugates are excreted in urine at several to 60 mg/day in women and at 200 to 400 mg/day in pregnant women.

The national survey conducted by the Ministry of the Environment in 2005 (17th year of Heisei) reported that E2 possessing the highest estrogenic activity among estrogens was detected at concentrations of 0.11-1.7 ng/L in 4 out of 11 examined spots. Natural estrogens are supposed to affect the ecologic system at a concentration as low as several ng/L.

In Japan, the removal rate of estrogens at sewage treatment plants vary greatly depending on treatment plants and their environments. Development of treatment methods that can remove estrogens highly efficiently as well as stably is now desired. Currently, advanced sewage treatments including ozonization and activated carbon treatment are now being carried out.

Regarding E2, there are reports on adsorption treatment by activated carbon²⁾, removal efficiency improved by a

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combination of ozone and hydrogen peroxide³), and removal of 90% or more attained by ozone-induced degradation⁴⁻⁹. Ozonization can remove easily and nearly completely persistent organic substances, dyes, and malodorous substances which used to be imperfectly disposed by chlorination. Activated carbon, on the other hand, is said to have a variety of functional groups on the surface and to exhibit catalytic actions^{10,11}. There is a report that water polluted by dyeing could be more efficiently decolorized by one-process treatment, in which activated carbon was simultaneously added at the time of ozonization, than two-process treatment in which activated carbon treatment followed ozonization¹². However, because E2 exists at a low concentration in sewage water and because it is a hydrophobic substance, its removal is considered to differ from decolorization of dye-polluted drainage water. It is therefore necessary to assess validity of ozonization combined with activated carbon in removal of the hormone.

In this paper, we studied a new advanced type of treatment, namely, a method that used coincidentally ozone and activated carbon, in which activated carbon was added at a step of ozone treatment, and evaluated its capability to remove E2.

2 EXPERIMENTAL

2.1 Experimental conditions

Authentic E2 was purchased from Wako Pure Chemical Industries, Ltd. and it was dissolved in a mixture of acetonitrile and water (55:45). Quantitative determination of E2 was made with the use of a high-performance liquid chromatograph (LC-10A, SHIMADZU) under the conditions: column, 4.6 mm × 250 mm CAPCELL PAK C18 SG120 S5 (Shiseido Co., Ltd); mobile phase, acetonitrile:water = 55:45; flow rate, 0.8 mL/min; column temperature, 40°C; and wave length, 210 nm.

2.2 Activated carbon

We used activated carbon graded as chromatography use after sieving it to get 63-297 μm sized particles. The carbon's weight loss on drying at 105°C was up to 15%. The activated carbon was treated with ozone as follows. Five g of the carbon were suspended in 200 mL of purified water. The suspension was aerated with 2.0 or 6.0 kg of ozone, followed by its filtration to collect the carbon particles, which were dried thereafter. The amount of ozone consumed for the actual treatment was 26 g or 516 g.

Ozone was generated from oxygen gas (Iwatani GAS) using an ozone generator (OKANO WORKS, LTD.). The generation rate of ozone (g/min), which was captured in KI solution, was determined by titration with 0.1 mol/L $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Capacity for iodine adsorption was determined as an

index of specific surface of activated carbon. This capacity (mg/g) of activated carbon was determined according to the JIS K1474 procedure designed for the carbon as follows. Activated carbon was put in 50 mL of 0.05 mol/L iodine solution (for volumetric analysis) and the suspension was shaken for 15 min at 25°C, followed by suction filtration through 0.45 μm membrane filters (Toyo Roshi Kaisha, Ltd.). The filtrate was titrated with 0.1 mol/L $\text{Na}_2\text{S}_2\text{O}_3$ solution to assess the capacity (mg/g).

Base consumption by activated carbon was measured by the method of Boehm *et al.*^{13,14} Briefly stated, 1.0 g of activated carbon was suspended in 100 mL of 0.1 mol/L NaOH solution and the suspension was shaken for 48 h at 25°C, followed by suction filtration using 0.45 μm membrane filters. Fifty mL of the filtrate was titrated with 0.1 mol/L HCl solution to determine the base consumption.

2.3 Adsorption of E2 onto activated carbon

Rates of E2 adsorption onto activated carbon were measured as follows. Two and a half mg of activated carbon was put in a microtube containing 1.5 mL of 20 mg/L E2 solution. The microtube content was filtrated through a 0.45 μm membrane filter at various lapse times and the filtrate at each time was determined for E2 concentration. In addition, the removal rate of E2 by activated carbon was determined as follows. A half to five mg of activated carbon was put in E2 solution with initial concentrations varying from 0.67 to 20 mg/L and the suspension was shaken for 60 minutes, followed by filtration through a 0.45 μm membrane filter. The filtrate was measured for equilibrium E2 concentration. In order to evaluate ozone effects on activated carbon, ozonized activated carbon was similarly processed to measure the equilibrium concentration and to calculate the removal rate of E2.

2.4 E2 degradation by ozone

Two hundred mL of 100 mg/L E2 solution was put in an Ichinose-type gas washing bottle, which was aerated with ozone at a rate of 15 mL/min for 0 to 25 min. Ten mL aliquots of the specimen sampled at appropriate time points were measured for E2 concentration to calculate an apparent removal rate.

2.5 E2 degradation by ozonization in the presence of activated carbon

Two hundred mL of 100 mg/L E2 solution and 1.0 g of activated carbon were put in an Ichinose-type gas washing bottle, which was aerated with ozone at a rate of 20 mL/min for 0 to 60 min. Ten mL aliquots of the specimen sampled several times during the aeration time were measured for E2 concentration to calculate an apparent removal rate. A pH meter (METTLER TOLEDO Co.) was used for pH measurement. Furthermore, chemical oxygen demand (COD) was measured by the acid high-temperature

permanganic acid method. Briefly, 7.5 mL of 20% AgNO₃ solution, 5 mL of 30% H₂SO₄ solution, and 5.0 mL of 0.005 mol/L KMnO₄ were accurately added to 50 mL of the specimen, which was heated in water bath. The specimen was thereafter decolorized with 0.0125 mmol/L Na₂C₂O₄ solution, being titrated with 0.005 mol/L KMnO₄ solution. A total volume in mL of 0.005 mol/L KMnO₄ solution expended for the titration before and after ozonization represented 'a'. Similar volume obtained in a blank experiment gave 'b'. The titer of 0.005 mol/L KMnO₄ solution is F. COD was calculated by the following formula using these 'a' and 'b' values.

$$\text{COD}(\text{mg/L}) = 0.2 \times (a-b) F \times 1000 / \text{specimen volume (mL)} \quad \dots\dots\dots(1)$$

3 RESULTS AND DISCUSSION

3.1 Solid state properties of activated carbon

Surface solid state properties and capacities to adsorb iodine of non- and ozone-treated activated carbon are shown in Table 1. As is seen in the Table, ozone-treated activated carbon consumed more bases than non-treated one. It was noteworthy that activated carbon treated with 6.0 kg of ozone showed an increment of 10% in the base consumption as compared to non-treated one. Base consumption is an index of carboxyl group and phenolic hydroxyl^{13,14}. It was therefore considered that ozone oxygenated the surface of activated carbon to get carboxyl groups and phenolic hydroxyls increased. It was reported that ozone produced highly reactive hydroxyl radicals¹⁵. It was therefore assumed that adsorption of E2 was blocked through enhanced surface polarity because of the hydrophobic property of the hormone.

Iodine-adsorbing capacity of activated carbon is an index of specific surface area. Such capacity of activated carbon that had been pretreated with 6.0 kg ozone was found to be increased by 10% compared to that of non-pretreated one

as was the case with increased consumption of bases. It was therefore assumed that activated carbon treated with ozone had functional groups on the surface oxygenated and fine pores were formed. However, there was no change in the consumption of bases per unit surface area.

3.2 Adsorption of E2 onto activated carbon

Adsorbing rates of E2 onto activated carbon are shown in Fig. 1. The removal rates increased markedly until 20 min of adsorption initiation when the rates achieved equilibrium. This indicated that activated carbon could accomplish the removal of E2 in a very short time. Therefore, we set a shaking time at 60 min in the adsorption experiments of activated carbon.

The removal rates of E2 differing in initial concentrations by non-treated activated carbon are illustrated in Fig. 2. As shown in the figure, the removal rates increased as the initial E2 concentration decreased and as the amount of added activated carbon increased. It was reported that the amount of E2 adsorbed onto activated carbon depended on the distribution of fine pores, into which E2 was sup-

Fig. 1 Removal Rate of E2 by Untreated Activated Carbon.

Fig. 2 Removal Percentage of E2 by Untreated Activated Carbon.

Table 1 Properties of Activated Carbons.

Activated Carbons	Base Consumption (mmol/g)	Adsorption Capacity of Iodine (mg/g)
Untreated Activated Carbon	0.415	600.0
Activated Carbon Treated with Ozone (2kg)	0.455	610.1
Activated Carbon Treated with Ozone (6kg)	0.465	666.0

Fig. 3 Removal Percentage of E2 by Activated Carbons.

posed to be adsorbed, because of the hydrophobic property of the hormone⁵. The same mechanism of adsorption onto activated carbon seemed to work in the carbon used in the present study.

We have shown that ozone has an oxidizing power potent enough to alter functional groups on the surface of activated carbon. Moreover, since ozone generates highly reactive hydroxyl radicals on the surface of activated carbon¹⁵, it is conceivable that functional groups existing on its surface affect E2 adsorption onto the carbon. The adsorption rates of E2 onto ozonized activated carbon are given in Fig. 3 which indicates practically no difference in the removal rate between non- and ozone-treated activated carbon. So, as is shown in Table 1, ozone treatment may alter specific surface area as well as surface polarity of activated carbon but did not influence E2 adsorption. These results and a study reporting E2 adsorption into fine pores of activated carbon²) prompted us to examine whether hydroxyl radicals generated on the surface of activated carbon influenced E2 degradation. Our results indicated that ozonized activated carbon did not reduce the amount of removed E2 despite changes of solid state properties caused by the radicals.

3.3 E2 degradation by ozone

The removal rates of E2 by ozone treatment or by ozone treatment combined with activated carbon are shown in Fig. 4. The removal rates increased in proportion to treatment time and E2 degradation was completed in about 25 min under the current conditions. On the other hand, a smaller amount of ozone was required to break down E2 when activated carbon was combined than when ozone alone was introduced, indicating E2 degradation singly by ozone and E2 removal by activated carbon simultaneously going on. Since ozone was reported to work as an adsorbent and also as a catalytic agent as well in the ozone treatment of dyes together with activated carbon¹⁶), similar reactions might have taken place in the case of E2.

Fig. 4 Removal Percentage of E2 by Ozone or Ozone Treatment with Activated Carbon.

Fig. 5 Removal Percentage of E2 by Different Three Treatments.

Activated carbon in aqueous solution is able to convert ozone to hydroxyl radicals¹⁷. It is therefore assumed that added activated carbon increased the amount of hydroxyl radicals, those were required for E2 decomposition, resulting in enhancement of the removal rate. Moreover, activated carbon has a variety of functional groups on its surface, which may accelerate ozone-induced E2 decomposition. Therefore, there is a possibility that E2 is removed in a shorter time by a combination of ozone and activated carbon and that two processes of ozone and activated carbon treatments can be integrated into one process. To achieve this operation, production as well as behaviors of by-products of ozonization in the presence of activated carbon needs to be studied.

The time courses of the removal rates of E2 in treatments with ozone alone, activated carbon alone, and ozone combined with activated carbon are shown in Fig. 5. The ozone treatment combined with activated carbon removed E2 more rapidly than that with ozone alone or activated carbon alone. On the other hand, the removal rates were

Fig. 6 Change of Chemical Oxygen Demand and pH in E2 Solution by Different Three Treatment.

higher in the activated carbon-ozone treatment or in the ozone treatment than in the treatment with activated carbon alone. Hence, it was clarified that the ozone treatment in combination with activated carbon accelerated the E2 removal rate, could finish in a shorter time, and enhanced the decomposition rate. Conceivably, as mentioned above, ozone in aqueous solution generates hydroxyl radicals which were produced in a larger amount by adding activated carbon leading to an increase of the removal rate, while activated carbon adsorbs the hormone concomitantly.

Figure 6 shows COD values after E2 removal as well as changes of pH. In the treatment with ozone alone, the COD values were decreased probably because ozone degraded E2 into small-molecule moieties by oxidative decomposition. On the other hand, COD values abruptly declined at 10 min after treatment initiation and increased later in the treatment with ozone combined with activated carbon or in that with activated carbon alone. It was possible that a micronized fraction of activated carbon increased COD values. These results suggest that ozone treatment combined with activated carbon has an advantage of shortening the processing time down to about 10 min but long treatment increases COD values, necessitating determination of the most appropriate treatment time.

On the other hand, when E2 was treated with ozone or ozone combined with activated carbon, the pH declined abruptly immediately after treatment initiation and reached a plateau value of around 4 later at 15 min. The treatment with activated carbon alone resulted in a plateau value of around pH 5, indicating decomposition of E2 to high polar acid moieties by the treatment with ozone alone or in combination with activated carbon. In other words, conceivably, E2 is decomposed by ozone molecules almost at the same time as the ozone treatment is started and various weakly acid polar moieties are produced, while E2 is adsorbed and pH changes a little in the case of treatment with activated carbon.

4 CONCLUSION

The removal rates of E2 by treatment with activated carbon were proportional to the amount of activated carbon. Surface polarity and specific surface of activated carbon were changed by ozone but the E2 removal rates were not. In contrast, ozone completely decomposed and removed E2. Ozone removed a greater amount of E2 in a shorter time in combination with activated carbon than ozone alone. The long treatment was associated with an increase of the COD values, indicating the necessity of setting up the most appropriate treatment time.

It was found from these results that activated carbon, if added to treatment with ozone, contributed to reduction of treatment time, which had to be adjusted properly. Treatment with ozone combined with activated carbon proved to be applicable to hydrophobic material like E2 besides hydrophilic substances like dyes, having a potential to become highly efficient water processing technique. In an attempt to apply these treatments to field works, it is necessary to study by-products and their behaviors and to evaluate the treatments in realistic settings including E2 concentrations to be detected in the real world and the practical amount of activated carbon to be used for concrete treatment.

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