Synergetic Effect of Ultrasound Irradiation in the COD Removal and Degradation of L-ascorbic acid in Aqueous Solution by Aerobic Treatment.

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ABSTRACT

The ultrasound irradiation and simultaneous oxygen bubbling into the L-ascorbic acid aqueous solution has been studied in order to establish a cost-effective oxidation process for wastewater treatment. The application of ultrasound considerably increases the decomposition rate, while the relative chemical oxygen demand (COD) value is essentially unchanged. The influence of various process parameters, such as temperature and oxygen flow rate, has been studied. Moreover, we have carried out preliminary experiments on the influence of the addition of metal oxide particles, i.e. SiO_2 and TiO_2. The effects of particles on the degradation of AH_2 and the COD compounds are discussed.

Keywords: ultrasound, aerobic oxidation, L-ascorbic acid, decomposition, COD

1. INTRODUCTION

L-ascorbic acid (AH_2) or vitamin C is essential in the human body as an antioxidant. The reagent is also used in industries as a food additive or reducing agent for precious metal production /1/. The discharge of wastewater containing organic compounds causes the problem of the increase of the chemical oxygen demand (COD) in the surrounding water environment. Many techniques have so far been studied for the removal of COD compounds in wastewater, e.g. plasma treatment and activated sludge method. In the case of AH_2-containing aqueous solution, aerobic oxidation at high temperature is known to be a powerful method to degrade AH_2. However, it is of importance to develop a more effective treatment method to save the treatment cost and energy. A possible candidate is to utilize sonochemical method which is based on the acoustic cavitation /2, 3/. The cavitation phenomenon causes the decomposition of water molecules due to the violent collapse of cavitation bubbles, which reaches up to the temperature of several thousands kelvin and ~1000 atm. To the authors' knowledge, however, there are few studies on the sonochemistry of the decomposition of AH_2. One of the reasons is that the AH_2 is a strong antioxidant against e.g. hydroxyl radical (·OH), the most effective oxidants among the sonochemical products of water, can be easily scavenged.

In the present work we have studied the effect of ultrasound irradiation and the simultaneous oxygen bubbling for the oxidative decomposition and removal of COD compounds in the AH_2 aqueous solution. It is expected that a combination of ultrasound and oxygen bubbling can cause both physical and chemical influences in addition to the conventional aerobic

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oxidation. The former is based on the strong mixing effect of the oxygen bubbles by the ultrasound irradiation as well as the increase of the apparent bubble surface area due to the breakup of bubbles /4/. The latter is related with the formation of more reactive oxidants such as hydroperoxyl radical ($HO_2\cdot$) and ozone /2/. On the other hand, bubbling of gases into sound field causes the attenuation of the sound, so that only a few works have been so far reported in literature with respect to the wastewater treatment /5, 6/. In the present paper we have examined how to optimize the experimental parameters such as oxygen gas flow in order to cope with the problem of the sound wave attenuation and to achieve the highest efficiency of ultrasound irradiation.

The addition of particles can enhance the oxidation of organic compounds in water. The addition of titanium oxide into sonicated solution is especially interesting with respect to the synergetic effect of sonochemistry and photocatalysis. Tuziuti *et al.* suggested the formation of reactive oxidants at particle surface sites, e.g. TiO_3 and $TiOH^+$ species in the presence of TiO_2 particles under sonication /7/. A recent study by Nakajima *et al.* suggests that thermally excited holes on TiO_2 surfaces are responsible for the enhancement of the decomposition of 1,4-dioxane in aqueous solution /8/. We have, therefore, also studied the influence of the TiO_2 as well as SiO_2 particles in the ultrasound field and the oxygen bubbling.

2. EXPERIMENTAL PROCEDURE

As for the materials, reagent grade of AH_2, supplied from Wako pure chemical, TiO_2(rutile) and SiO_2, supplied from Kojundo Chemical Laboratory (BET surface area: 1.8 m^2/g for TiO_2 and 0.9 m^2/g for SiO_2), were used without any further purification. The sample solution was prepared by dissolution of the proper amount of AH_2 into the distilled water. The experimental set-up is schematically shown in Fig. 1. The ultrasound system consists of a stainless steel horn and a sonifier (Telsonic, RS-20-48-02 type horn and MRG-20-1400R sonifier). The sound frequency is 20 kHz, and the input electric power is 700 W. The horn was immersed in a water bath made of acrylic resin with diameter of 200 mm and the height of 200 mm. The temperature of the water bath was controlled within ±1 K. Ultrasound was irradiated from the vertical side of the sample cell of pyrex glass (a.d. 30 mm, i.d. 26 mm), which is closely situated to the horn with the help of an aluminum holder. An indirect irradiation of ultrasound to acidic solution has the advantage of avoiding the possible corrosion of sonifier. On the other hand, a disadvantage with respect to the attenuation of ultrasound energy cannot be prevented: a calorimetric experiment, based on the method described by Koda *et al.* /9/, showed that ca. 1 % of the input electrical energy was transformed into the inside of the sample cell.

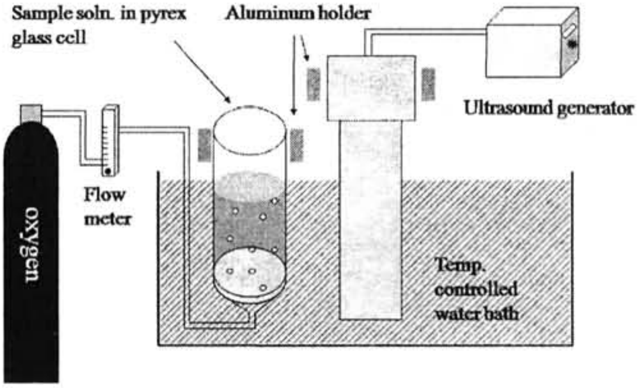

Fig. 1: Schematic experimental set-up for ultrasound irradiation and the simultaneous oxygen bubbling.

Oxygen gas was bubbled from the bottom of the cell through a porous plate. The sparger has the apparent pore size of 100-120 μm. During sonication and bubbling treatment 2 milliliters of the solution were sampled at appropriate time intervals, and the concentration of AH_2 in the solution was measured spectrophotometrically by absorbance at the wavelength of 252 nm with a UV-VIS spectrometer (Shimadzu, UV-VIS 2500). The COD of the sample solution was evaluated by the reaction with potassium permanganate as oxidant /10/. The oxidation reaction was carried out for 30 min at 373 K, and the amount of the remaining $KMnO_4$ was determined by the change in absorbance at the wavelength of 525 nm. Thus, the COD value can be estimated by the change in absorbance before and after the oxidation reaction. In the case of the treatment with oxide addition, the particles were removed by a centrifuge with the rotating speed of 3000 rpm for 5 min, and the upper clear solution was used for the analysis of AH_2 content and the COD. The experimental error of the COD value determined by this method was ~ 20 %.

3. RESULTS AND DISCUSSION

3.1 Simultaneous treatment of ultrasound irradiation and oxygen bubbling

Fig. 2 exhibits the change in the concentration of AH_2 represented by the absorbance ratio of the solution, A/A_0, i.e. (absorbance $_{252\ nm}$ at time t / absorbance $_{252\ nm}$ of the initial sample). The experimental conditions are shown in the figure. Essentially no change in the absorbance was observed in the case of simple oxygen bubbling, while a subtle decrease was found in the case of heating treatment. It is well known that AH_2 decomposes at high temperature. However, the present result shows that the influence of decomposition due only to the temperature increase is not crucial because the temperature of water bath in the major experiments of the present research is less than 323 K. On the other hand, oxygen bubbling at high temperature exhibits high degradation rate with zero-order kinetics, as demonstrated in Fig. 2. This result shows that the aerobic oxidation at high temperature is an effective method for the decomposition of AH_2. As shown in the figure, the irradiation of ultrasound is also effective for the decomposition, and simultaneous bubbling of oxygen results for the enhancement of the decomposition rate. In comparison with the aerobic oxidation at 313 K without sonication, the decomposition behavior is different in the case of oxygen bubbling plus ultrasound. This can be interpreted also by the increase of the temperature during the treatment. Thus, in the following experiments the temperature of the water bath was controlled within 1 K.

Fig. 3 shows the results of AH_2 decomposition at different temperatures. The concentration of AH_2 decreases linearly with treatment time. The decomposition rate increases with increasing temperature up to 313 K, and then decreases slightly at 323 K. On the one hand, the degradation accelerates with increasing temperature. On the other hand, the effect of cavitation decreases because much vapor comes into the bubbles at higher temperature, resulting in the cushioning effect of the violent collapse /2/. The present observation results from the competition of both effects. It should be noted that most of sonochemical reactions exhibits optimum reaction temperature /2/.

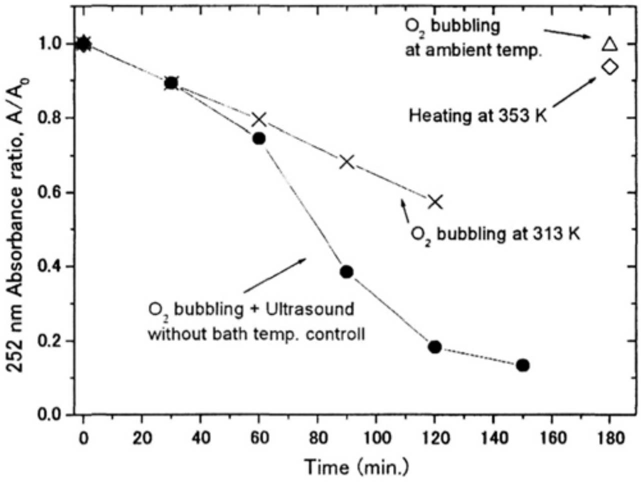

Fig. 2: Comparison of decomposition behavior of AH_2 by various treatments.

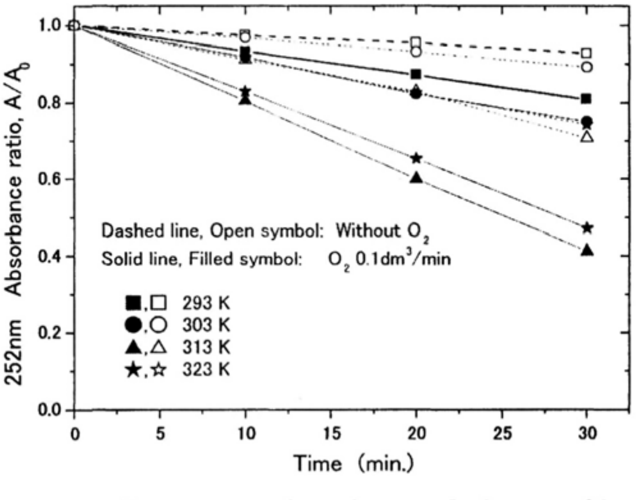

Fig. 3: Temperature dependence of decomposition behavior of AH_2.

As mentioned in the introduction, the optimization of experimental parameters with respect to the gas sparging is an important issue. We have therefore explored the change in absorbance at various oxygen flow rates. The results are shown in Fig. 4. The decomposition rate increases with increasing the flow rate up to 0.1 dm^3/min, while significant change is not observed above 0.1 dm^3/min. The increase in the flow rate results in the increment of the formation rate of gas bubbles in solution. On the other hand, the mean gas bubble size increases with increasing gas flow rate so that the residence time decreases. It should be also considered that the increase in the volume of bubbles with respect to that of solution can block the transmittance of the ultrasound energy. Thus, the increase in flow rate does not straightforwardly lead to the increase in the decomposition rate. The present result can be understood by the competitive effect of the above-mentioned effects. The obtained results show that the flow rate of 0.1 dm^3/min is sufficient to achieve the highest decomposition rate in the present experimental configuration.

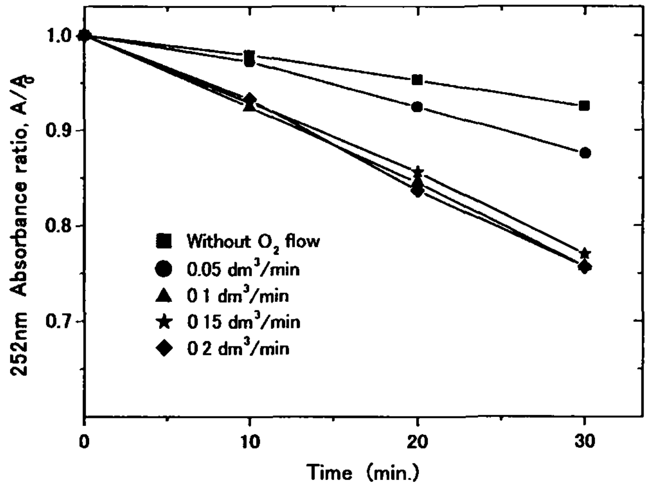

Fig. 4: Influence of oxygen flow rate on the AH_2 decomposition at 303 K under sonication.

It is of special interest to see if the present process is effective for the removal of COD compounds. Fig. 5 shows the change in COD by the simultaneous treatment of ultrasound irradiation and oxygen bubbling as a function of treatment time. The COD value remains essentially constant after the treatment of 3 hours.

In summary, the irradiation of ultrasound in aerobic treatment leads to the significant increase in the decomposition rate of AH_2, and several process parameters have been optimized. However, stronger oxidation process is required for the removal of COD in AH_2 solution.

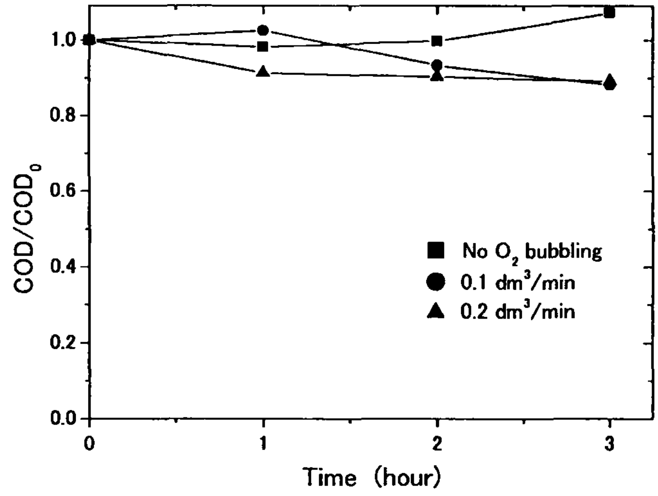

Fig. 5: COD change at 313 K with different oxygen flow rates.

3.2 Influence of the addition of oxide particles

In order to enhance further oxidation of the organic compounds we have studied the influence of the metal oxide particles added in the solution. Fig. 6 shows the change in AH_2 concentration by the simultaneous treatment of ultrasound and oxygen bubbling under the presence of SiO_2 and TiO_2, together with the results without ultrasound, i.e. oxide addition and gas bubbling. The interpretation of data is complex because many factors such as adsorption of AH_2 onto the particles as well as the catalytic decomposition of AH_2 by metallic compounds are involved that are related to each other.

In the case of treatment without ultrasound, it is clearly seen that the addition of oxide particles significantly increases the decomposition rate of AH_2 by the treatment of oxygen bubbling. It is known that the autooxidation of AH_2 increases considerably in the presence of trace amount of metal ions, such as Cu(II) and Fe(III) /1/. The addition of SiO_2 is especially effective for the degradation of AH_2. The detailed effect of the oxide as well as the examination of other oxides will be studied in our future project.

The irradiation of ultrasound in addition to the oxygen bubbling in the presence of oxide enhances slightly the AH_2 degradation in comparison to the results without ultrasound. Thus, taking the results without particles into account, we can conclude that ultrasound plays a minor role with regard to the decomposition of AH_2 in the case of oxygen bubbling under the presence of particles. One of the advantages of particle addition in ultrasound field is that particles serve as cavitation sites /2/. However, the attenuation of sound wave is presumably significant in the present experimental conditions. Moreover, the degradation behavior does not clearly correlate with the BET surface area, which can relate to the number of cavitation sites on the particle surface, of the oxides examined in the present study.

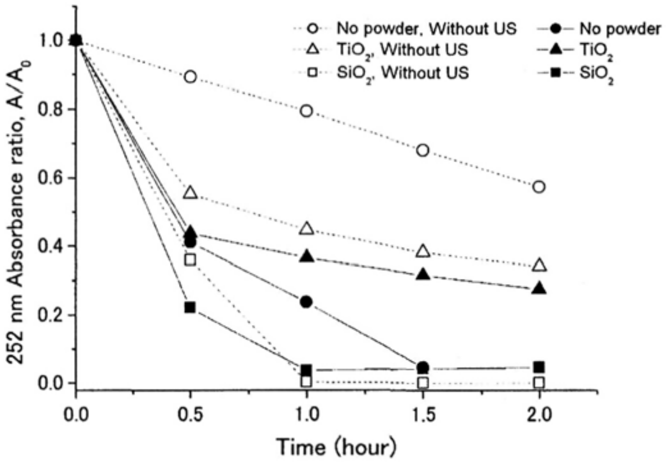

Fig. 6: Influence of the addition of SiO_2 and TiO_2 on the decomposition of AH_2 at 313 K. The powder concentration is 50 g/dm^3. The oxygen flow rate is 0.2 dm^3/min.

As for the COD, the addition of SiO_2 does not exhibit a significant decrease in the treatment without ultrasound, while the irradiation of ultrasound can slightly enhance the decomposition of COD compounds, as shown in Fig. 7. A striking observation is that the addition of titanium oxide results in the significant reduction of COD value even without ultrasound irradiation. The COD decrease of ca. 70% was observed after 1-1.5 hours of treatment. Further addition of the oxide to the concentration of 50 g/dm^3 after 1 hour treatment gave rise to the COD value of almost zero. Thus, the addition of oxide is obviously effective for the complete oxidation of AH_2. It is here noted that the decrease in AH_2 corresponds fairly well to that in COD value. Thus, ascorbic acid is immediately mineralized by the aerobic oxidation treatment with TiO_2 addition. The detailed mechanism is, however, unclear yet. Oxidative species formed at oxide surface can be responsible, although other factors such as adsorption should be considered.

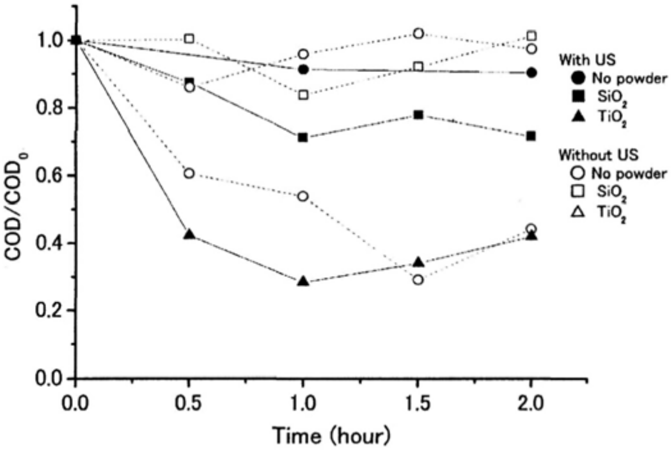

Fig. 7: COD change by the addition of metal oxide at 313 K. The powder concentration is 50 g/dm^3. The oxygen flow rate is 0.2 dm^3/min.

The irradiation of ultrasound into O_2 bubbling plus TiO_2 enhances the COD removal at the beginning of the treatment (< 1 hour). In the case of SiO_2, slight decrease of COD value was observed by the simultaneous ultrasound treatment. Further studies should be carried out in order to clarify the influence of metal oxide, since many factors are involved: for example, the mean particle size of the oxide decreased from 2.2 to 1.6 µm after the ultrasound irradiation for 2 hours, that can lead to the increase of the cavitation sites.

4. CONCLUSION

In the present study we have investigated the ultrasound irradiation and the simultaneous oxygen bubbling. The synergetic effect was observed with respect to the decomposition rate of AH_2 in comparison with each treatment alone. Several process parameters such as reactor temperature and gas flow rate have been optimized in the present experimental setup. The removal of COD was, however, not observed by this treatment. The addition of metal oxide particles was examined in aerobic oxidation with and without ultrasound irradiation. The presence of oxide changes both the decomposition rate and the COD removal behavior. The decomposition rate is increased substantially by the addition of SiO_2, while the COD compounds are fully removed by the addition of TiO_2.

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