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Wet electrolytic oxidation of organic pollutants in wastewater treatment

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Abstract

Wet electrolytic oxidation of organics in the presence of electrolytes and externally added oxygen gas was investigated for wastewater treatment. The experimental apparatus was a 300 ml electrolytic batch autoclave operated mainly at 250 °C and 7 MPa. The results showed that the presence of halide ions such as chlorides and bromides strongly catalyses the conversion of pollutant organic compounds to innocuous compounds such as CO_2 and water. The addition of external oxygen gas in wet electrolytic oxidation of acetic acid strongly suppressed the cathodic evolution of hydrogen gas and demonstrated a TOC removal profile with an apparent current efficiency higher than 100% for high concentration acetic acid solutions.

1. Introduction

Incineration is one possible process for the disposal of industrial organic wastewater which cannot be easily treated by biological processes. However, incineration methods pose problems of emissions if the conditions are not perfectly controlled, and a large amount of fuel is required for dewatering and burning the wastewater. Hydrothermal oxidation processes, such as wet oxidation [1–5] and supercritical water oxidation (SCWO) [6], have been proposed as alternative methods in which no dewatering is required. The former is usually operated at 180 to 320 °C and 7 to 18 MPa, and the latter at 400 to 650 °C and 20 to 30 MPa, both in the presence of a pressurized oxidant such as oxygen or air. In these systems, the pollutant organics in the wastewater are converted to innocuous compounds, such as CO_2 and water, under high-temperature and high-pressure aqueous conditions. These hydrothermal oxidation technologies are currently available as commercial processes.

On the other hand, electrochemical oxidation processes [7–14], usually operated at atmospheric pressure and temperatures up to 80 °C, have also been proposed for the treatment of certain industrial effluents. Electrochemical oxidation of phenol using special catalytic anodes, chloride ion catalysts or electrochemically generated Fenton's reagent was widely studied. However, it is recognized that electrochemical techniques encounter difficulties when it comes to achieving complete oxidation of the organic species [13]. Electrochemical oxidation at low temperature, in practice, is a slow reaction as a consequence of its kinetic rather than thermodynamic limitations [9]. Consequently, rapid and efficient electrochemical oxidation is expected with the use of high-temperature, pressurized electrolytic systems [10]. However, few studies on electrolytic oxidation under hydrothermal conditions have been reported.

The main purpose of this work is to evaluate the electrolytic oxidation of organics under hydrothermal conditions, by using a one-compartment electrolytic autoclave. We refer to this process as wet electrolytic oxidation (WEO). We have investigated WEO in terms of the reaction safety, the reaction-controlling parameters, the possible reaction scheme, the current efficiency and the oxidation characteristics of certain organic compounds. In this WEO study, we have given special emphasis to the oxidation of acetic acid, which is well known to be one of refractory compounds in conventional wet oxidation.

2. Experimental details

2.1. *Materials and methods*

Aqueous electrolyte solutions were prepared by dissolving commercially available salts and organics in deionized water. Electrolysis was carried out inside a sealed 300-ml batch autoclave made of SUS 316 stainless steel, as illustrated in Figure 1. Half of the autoclave's inner volume (150 ml) was charged with aqueous electrolyte solution. A cylindrical platinum plate electrode (25 mm in diameter, 30 mm in length), coaxial to the autoclave inner wall (70 mm i.d.), was used as the anode. The autoclave wall was used as the cathode to promote cathodic protection of the autoclave from corrosion.

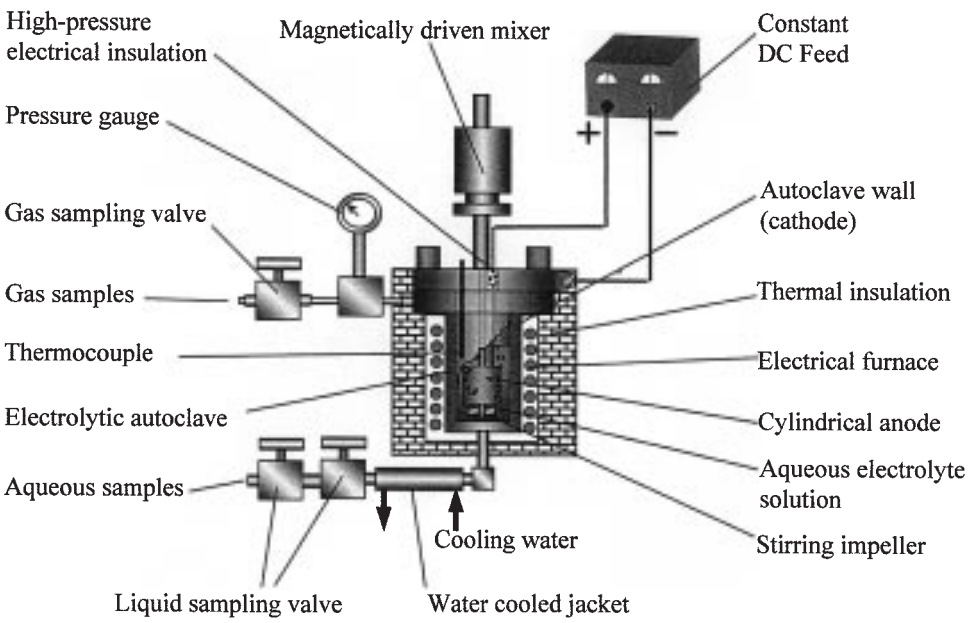

Fig. 1. Schematic illustration of experimental batch electrolytic autoclave.

The air in the autoclave, after charging the autoclave with aqueous solution, was purged with inert gas (argon) in all experiments. In wet oxidation and wet electrolytic experiments with oxygen gas added, oxygen gas was pressurized at a partial pressure of 1 MPa and then argon was added to make total pressure 3 MPa. For experiments without addition of oxygen gas, the autoclave was charged only with argon at 3 MPa. The total gas initially charged into the autoclave was always kept at 3 MPa and the existence of the aqueous phase was ensured for all temperatures below the critical point of water. The electrolyte solution inside the autoclave was continuously stirred throughout the experiment by means of a magnetically driven mixer. Temperatures and concentration were assumed to be uniform inside the autoclave. The sealed autoclave was heated with an electrical furnace from room temperature at a rate of approximately 400 °C per hour until the temperature, measured using a thermocouple inserted in the autoclave, reached the prescribed value. The inner pressure of the autoclave increased as a function of temperature, and the typical reaction pressure was 7 MPa when the autoclave temperature was 250 °C. Once the autoclave had reached the intended temperature, the prescribed constant electrical current (d.c.) was passed between the electrodes for wet electrolytic oxidation experiments. No current was passed for wet oxidation runs. The autoclave inner temperature was maintained at the prescribed temperature within an accuracy of ±0.5 °C, using a PID temperature controller.

2.2. *Analyses*

The reaction product yield of electrolysis was followed by the analyses of gases and liquids sampled from the autoclave. Sampled liquids were analyzed in terms of total organic carbon (TOC) and free residual chlorine (FRCl) concentrations. The concentration of free residual chlorine was assumed to be equivalent to that of hypochlorous acid resulting from the disproportionation reaction of chlorine with water. Chlorine was generated by the anodic oxidation of chloride ions in aqueous solution. Free residual chlorine was measured by the DPD (diethyl-*p*-phenylene diamine) colorimetric method. The gas composition in the autoclave was measured using TCD-equipped gas chromatograph. The TOC concentration was measured using SHIMADZU TOC 5000.

2.3. *Chemistry of the anodic oxidation and current efficiency*

The oxidizers formed during electrolysis of aqueous NaCl solution are hypochlorite (hypochlorous acid), chlorate (chloric acid) and oxygen [11]. Among them, hypochlorous acid was assumed to be the main oxidizer in this WEO investigation because of its high oxidation potential compared to the other oxidizer forms. In the case of acetic acid, the following reactions should occur in the electrolytic autoclave.

Oxidation of acetic acid by hypochlorous acid:

$$CH_3COOH + 4\,HOCl \rightarrow 2\,CO_2\uparrow + 2\,H_2O + 4\,HCl \tag{1}$$

Anodic hypochlorous acid generation:

$$8\,Cl^- + 4\,H_2O \rightarrow 4\,HOCl + 4\,HCl + 8\,e^- \tag{2}$$

Cathodic hydrogen gas evolution:

$$8\,H_2O + 8\,e^- \rightarrow 4\,H_2\uparrow + 8\,OH^- \tag{3}$$

The overall reaction becomes

$$CH_3COOH + 2\,H_2O \rightarrow 2\,CO_2\uparrow + 4\,H_2\uparrow \qquad (4)$$

The theoretically required electrical charge (Q^*, from Faraday's law) for the complete degradation of 1 mol of acetic acid is

$$Q^* = 8F = 772\,\text{kC} = 214.4\ \text{Ah}$$

The theoretical TOC (TOC_t) concentration was calculated from the above relation using

$$TOC_t = TOC_{initial} - (c_e/100)(itC_n)/(8FV) \qquad (5)$$

where $TOC_{initial}$ is the TOC concentration in the acetic acid electrolyte before applying d.c. between the electrodes, c_e is the current efficiency, i is the applied d.c. intensity, t is the elapsed time, C_n is the carbon weight per mol of acetic acid, F is the Faraday constant and V is the electrolyte volume.

The c_e was estimated by comparing the TOC_t value with the experimental TOC for a certain supplied charge (it). The value of c_e gives information about the oxidation mechanism in effect, in addition to the current efficiency. If the mechanism is purely anodic oxidation, c_e should be 100% when acetic acid is degraded at the ratio of 1 mol per 214.4 Ah. Values apparently higher than 100% might be obtained when other oxidation mechanisms are more dominant than anodic oxidation.

3. Results and discussion

3.1. *Hydrothermal aqueous NaCl solution electrolysis*

Exploratory electrolytic reactions with 2 wt % NaCl aqueous solution (no organics added) were carried out and the conditions under which a potentially explosive gas mixture accumulates inside the autoclave were investigated.

Figure 2 shows the concentration profile of gases and free residual chlorine (FRCl) inside the electrolytic autoclave for 2 A d.c. charged electrolysis, at various temperatures from 30 to 350 °C. The concentrations of hydrogen gas (Figure 2(a)), oxygen gas (Figure 2(b)), and free residual chlorine (Figure 2(c)) increased with time in electrolysis performed at temperatures up to 100 °C. However, electrolysis conducted at a high temperature (over 200 °C) always resulted in negligible yields of oxygen gas, hydrogen gas and FRCl. These product yields did not increase with electrolysis time. A possible reaction scheme that can explain this experimental result is that the oxidizer produced in the anode vicinity is again reduced at the cathode. The electrical energy consumed for electrolysis in this case seems to be transformed to thermal energy by the Joule–Kelvin effect and the electrochemical reaction irreversibilities. Therefore, electrolysis of aqueous NaCl solution under hydrothermal conditions, where hydrogen gas and oxygen gas evolution was remarkably suppressed, was found to be a safe reaction.

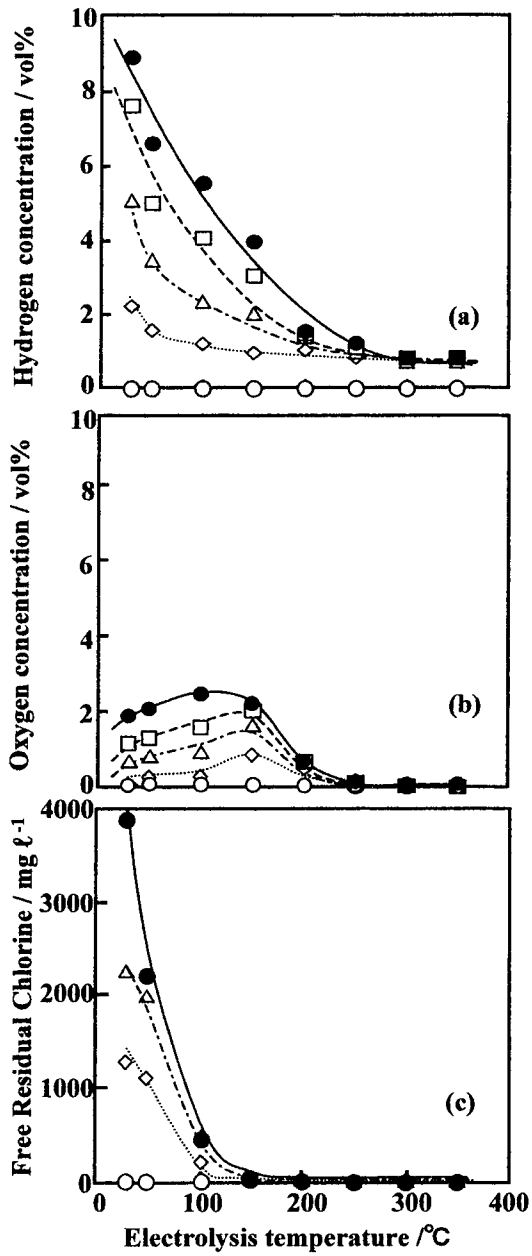

Fig. 2. (a) Hydrogen gas, (b) oxygen gas and (c) free residual chlorine concentration profile inside 300 ml autoclave in function of the electrolysis temperature when 150 ml of 2 wt % aqueous NaCl was charged. Conditions: $i = 2$ A. Initially charged gas: 3 MPa argon. Electroanalysis time: (○) 0, (◇) 15, (△) 30, (□) 45 and (●) 60 min.

3.2. *WEO of acetic acid*

Hydrogen gas suppression is of interest in view of process safety, but the suppression of oxygen and free residual chlorine could be problematic in performing an oxidation reaction. However, further WEO experiments with acetic acid in this reaction medium have shown clear progress in the oxidation reaction. Figure 3 shows the TOC (Figure 3(a)) and gas composition profile

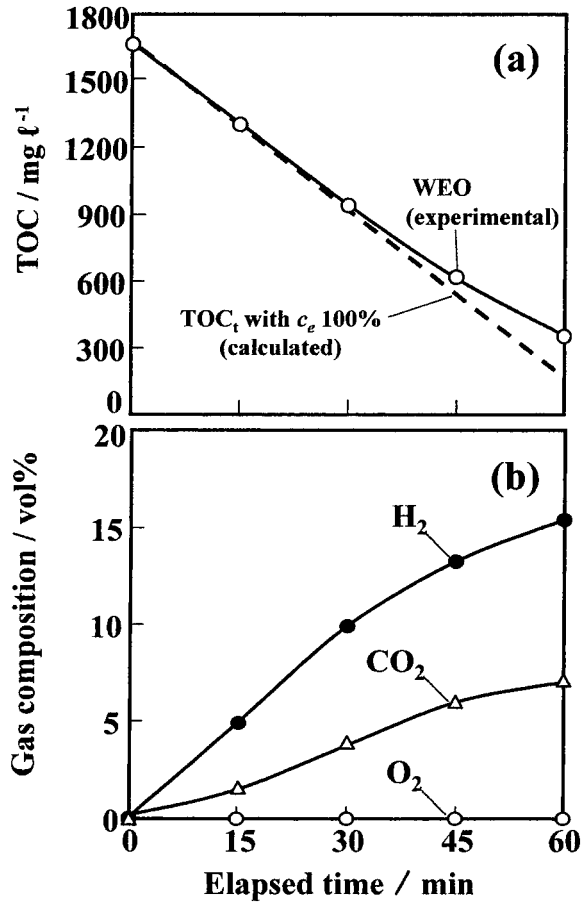

Fig. 3. (a) TOC and (b) gas composition profile for WEO of acetic acid. Conditions: $[\text{Acetic acid}]_{\text{initial}} = 4000$ mg l^{-1}, $V = 150$ ml, $T = 250\,°C$, $P = 7$ MPa, [NaCl] = 2 wt % and $i = 2$ A. Initially charged gas: 3 MPa argon.

(Figure 3(b)) for WEO of acetic acid at 250 °C. The gaseous products were in good agreement with overall Reaction 4. The volumetric (molar) ratio of CO_2:H_2 is 1:2. When acetic acid TOC concentration is higher than 900 mg l^{-1}, the experimental TOC is in good agreement with the theoretical TOC_t, using c_e as 100%. These results confirmed the validity of Reaction 4 and indicated an effective oxidation due to the anodic contribution. However, for lower TOC concentrations, the experimental TOC deviated from this TOC_t with 100% c_e. This is plausible since part of the oxidizer electrogenerated at the anode begins to be reduced at the cathode before reacting with acetic acid. Figure 3(b) also shows that the oxygen gas is not produced in this WEO. Hydrogen gas is produced in WEO of acetic acid because oxygen atoms of water are converted to CO_2. The remaining hydrogen atoms of the water molecule seem to be converted to hydrogen gas.

Although the overall reaction formula was in good agreement with experimental data, some uncertainties still remained concerning the electrochemical oxidation mechanism. Free residual chlorine was not detected for any liquid sample collected from the autoclave under this reaction condition. This indicates that if Reaction 1 is taking place in the electrolyte solution, this oxidation is an extremely fast reaction wherein all the electrogenerated hypochlorous acid is immediately consumed. Electrochemical oxidation of acetic acid directly on the anode surface, before hypochlorous acid or oxygen gas evolution, is another possible mechanism. The role of other oxidant species, such as chlorates, is unknown and further investigation is required to determine the exact mechanism.

3.3. *WEO with externally added oxygen*

Industrial organic wastewater is usually composed of a wide variety of organics. On the one hand, organics such as phenols can be easily degraded by wet oxidation with molecular oxygen supplied to the reaction medium by compressing air. On the other hand, organics such as acetic acid are negligibly degraded under wet oxidation conditions but are easily degraded in WEO, as described in the previous section. The production cost of electrochemical oxidizers is usually greater than the cost of just compressing the oxygen that is abundant in air. Thus, a combined hydrothermal oxidation that uses molecular oxygen and the electrochemical technique is of economic interest for wastewater treatment. For this reason, we have investigated the possibility of injecting molecular oxygen into the WEO media. However, here we must focus again on reaction safety, because we know that hydrogen gas is produced when some organic compounds are present in WEO. Combining WEO with wet oxidation means that oxygen gas must be injected into the high-temperature/high-pressure reactor where hydrogen gas is produced.

However, when we added oxygen gas from an external source during WEO, hydrogen gas evolution was greatly suppressed in the electrolytic autoclave experiment. Figure 4 shows the gas yield and TOC concentration profile for WEO of acetic acid with externally added oxygen. Initial acetic acid and NaCl concentrations and other conditions such as temperature and pressure are the same as in Figure 3, except that we initially charged the autoclave with 1 MPa oxygen gas and 2 MPa argon in place of 3 MPa argon. The observed c_e was 160% while the acetic acid TOC concentration was higher than 470 mg l^{-1}. In this Figure, we also plot the experimental TOC profile for wet oxidation (no current) of acetic acid. This experimental TOC profile slope corresponds to the 10% c_e of WEO with 2 A d.c. current. This indicates that, in WEO with externally added oxygen, direct oxidation by molecular oxygen may contribute an additional 10% of c_e. Therefore, the maximum achievable apparent c_e is 110%. The discrepancy with the experimentally observed c_e of 160% suggests that another reaction is taking place in addition to the anodic oxidation and the direct oxidation by molecular oxygen. Conversion of inactive molecular oxygen to active oxygen is one known cathodic reaction. This electrochemical reduction of molecular oxygen has been studied for hydrogen peroxide production [15–17] and *in situ* generation of Fenton's reagent [18, 19]. One

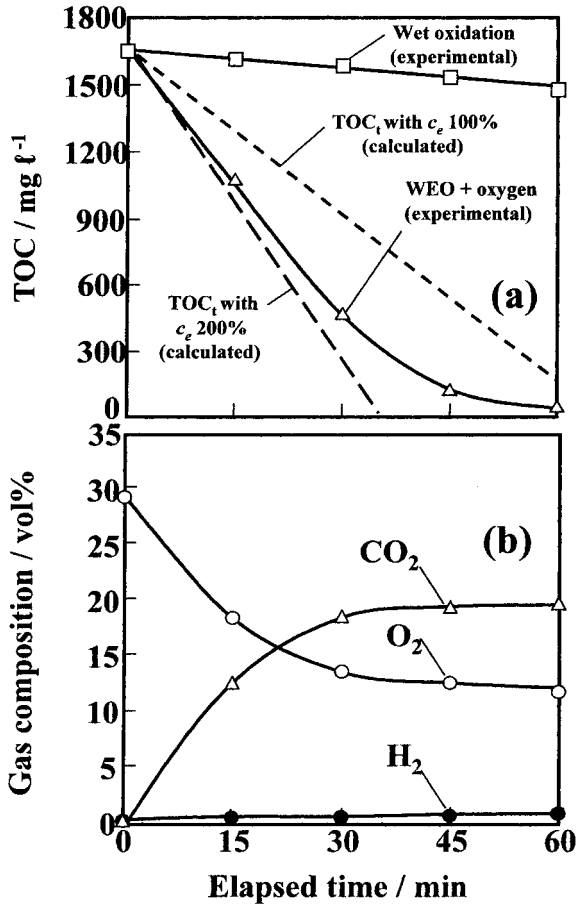

Fig. 4. (a) TOC and (b) gas composition profile for WEO of acetic acid in presence of externally added oxygen gas. Conditions: $[\text{Acetic acid}]_{\text{initial}} = 4000$ mg l^{-1}, $V = 150$ ml, $T = 250$ °C, $P = 7$ MPa, [NaCl] = 2 wt % and $i = 2$ A. Initially charged gas: 1 MPa oxygen and 2 MPa argon.

explanation for our experimental results is that similar electroreduction of externally added oxygen to active oxygen occurs in place of the cathodic evolution of hydrogen gas. Assuming that this cathodic electrogeneration of active oxygen occurs and this active oxygen reacts with acetic acid, the WEO of acetic acid with externally added oxygen gas can be written as follows.

Oxidation of acetic acid by hypochlorous acid:

$$CH_3COOH + 4\,HOCl \rightarrow 2\,CO_2\uparrow + 2\,H_2O + 4\,HCl \tag{6}$$

Oxidation reaction of acetic acid by active oxygen such as hydrogen peroxide:

$$CH_3COOH + 4\,H_2O_2 \rightarrow 2\,CO_2\uparrow + 6\,H_2O \tag{7}$$

Anodic hypochlorous acid generation:

$$8\,Cl^- + 4\,H_2O \rightarrow 4\,HOCl + 4\,HCl + 8\,e^- \tag{8}$$

Cathodic hydrogen peroxide evolution:

$$8\,H_2O + 4\,O_{2[aq.]} + 8\,e^- \rightarrow 4\,H_2O_2 + 8\,OH^- \tag{9}$$

The overall reaction becomes

$$2\,CH_3COOH + 4\,O_{2[aq.]} \rightarrow 4\,CO_2\uparrow + 4\,H_2O \tag{10}$$

According to the above reaction scheme, acetic acid can be completely degraded to CO_2 and water with an efficiency of 2 mol per 214.4 Ah. Reactions 6–10 explain the c_e value apparently higher than 100% and the suppression of hydrogen gas evolution.

3.4. *Influence of chloride ion concentrations in WEO*

The influence of chloride ion concentrations in WEO of acetic acid was investigated with a view to elucidating the catalytic effect and better understanding the oxidation mechanism. The chloride ion concentration was varied from 10.6 mg l^{-1} (usual tap water chloride ion concentration) to 12 100 mg l^{-1} (2 wt % NaCl), by charging different NaCl concentrations into the autoclave. The total supplied charge was kept constant at 2 Ah and three different current densities passed between the electrodes. Other conditions such as acetic acid concentration (4000 mg l^{-1}), reaction temperature (250 °C), reaction pressure (7 MPa) and initially charged gas pressure (1 MPa oxygen and 2 MPa argon) were the same for all runs discussed in this section.

Figure 5 shows that the TOC removal rate is independent of current density, if the total applied electrical charge is constant, for a wide range of chloride ion concentration. This Figure also shows that TOC removal rate is greatly enhanced by increasing the chloride ion concentration from 10.6 mg l^{-1} to 152 mg l^{-1}. A smooth increase in the TOC removal rate was observed for chloride ion concentration over 152 mg l^{-1}. This Figure shows that the chloride ion concentration is an electrochemical oxidation rate-limiting parameter in

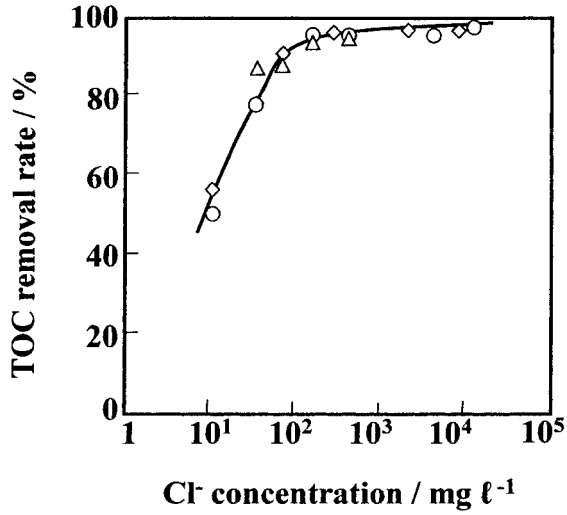

Fig. 5. Influence of chloride ions concentration on TOC removal rate. Condition: $[\text{Acetic acid}]_{\text{initial}} = 4000$ mg l^{-1}, $V = 150$ ml, $T = 250$ °C, $P = 7$ MPa and $Q = 2$ Ah. Initially charged gas: 1 MPa oxygen and 2 MPa argon. Total electrical charge: (◇) 1 A × 2 h, (○) 2 A × 1 h and (△) 3 A × 2/3 h.

WEO when its concentration is below 152 mg l^{-1}. Since oxygen gas was initially charged in all runs here, it was expected that the absence of chloride ions influenced only anodic oxidation reactions in which hypochlorous acid was assumed to be taking part (Reaction 6). However, the drastic decrease of the TOC removal rate when a low concentration of chloride ions, such as 10.6 mg l^{-1} was charged, suggests that chloride ions also plays some role in the cathodic conversion of molecular oxygen to active oxygen (Reaction 9) or in the oxidation reaction of acetic acid by active oxygen (Reaction 7). The catalytic mechanism in WEO with added oxygen gas is unknown, but the effects of chloride ion on WEO will be clarified in Section 3.7, where the catalytic effects of different electrolytes are discussed.

In this work, for better characterization of our WEO autoclave apparatus, the influence of chloride ion concentration on voltage (U) between the electrodes was also investigated. Voltage is not a rate-controlling parameter in the electrochemical reaction, but it directly influences the electrical power consumption.

Figure 6 shows the voltage between the electrodes as a function of time for different chloride ion concentration in WEO of 4000 mg l^{-1} of acetic acid at 250 °C with added oxygen gas. The measured voltage profile in Figure 6 is the voltage required to conduct 2 A d.c. in the present apparatus. For chloride ion concentrations as low as 10.6 mg l^{-1}, the voltage increased considerably with electrolysis time. This increase was attributed to the conversion of dissociated acetic acid in the electrolyte solution to the gas phase in the form of CO_2 as a consequence of the WEO reaction. For higher chloride ion concentrations, however, the voltage between the electrodes was influenced not by the amount of acetic acid in the electrolyte solution but depended on the initial concentration of chloride ions. The relationship between current and voltage in WEO of acetic acid at 250 °C with added oxygen gas is shown in Figure 7. From the straight section of the voltage vs current line for each chloride ion concentration in Figure 7, the electrical resistance between the electrodes and the voltage axis intersection (U_o) was calculated using linear regression. Results are plotted in Figure 8. The electrical resistance decreased with increase in chloride ion concentration, but U_o was constant for concentrations higher than 152 mg l^{-1}.

3.5. *Effect of current intensity on TOC removal profile*

Figure 9 shows the TOC and CO_2 profile in the autoclave for different currents in WEO of acetic acid with added oxygen gas. The investigated current intensity was in the range 0–6 A and other conditions were kept constant. The TOC decreased faster for higher currents. Once the theoretically electrical charge required for complete oxidation of a given amount of acetic acid is constant, fast oxidation is achieved if higher current intensity is applied. Although the TOC concentration is still high, a linear dependence of TOC removal on the electrical charge was observed.

3.6. *Effect of reaction temperature in WEO*

Figure 10 shows the TOC removal profile dependence on temperature in WEO with added oxygen gas. The WEO temperature was investigated from 100 to 300 °C and other experimental conditions were kept constant. For WEO at 100 °C, the TOC removal rate was slow and little increase of the CO_2 concentration was observed inside the autoclave. A clear increase in the TOC removal rate was observed with increase in reaction temperature. It was found that the minimum

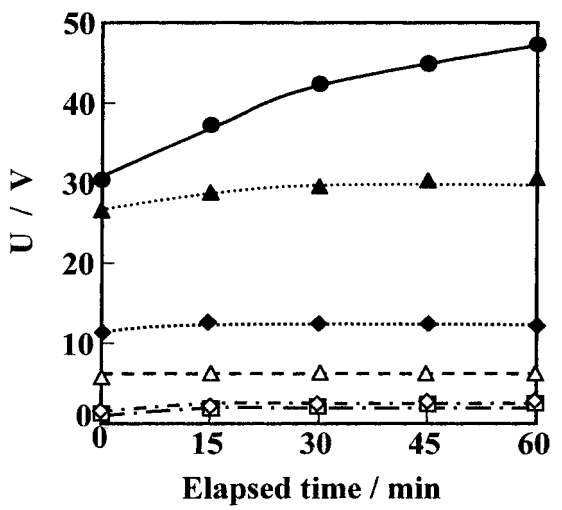

Fig. 6. Influence of chloride ions concentration on voltage (U) profile between the electrodes. Conditions: [Acetic acid]$_{initial}$ = 4000 mg l^{-1}, V = 150 ml, T = 250 °C, P = 7 MPa and i = 2 A. Initially charged gas: 1 MPa oxygen and 2 MPa argon. Chloride ion concentration: (●) 10.6, (▲) 32.0, (◆) 152, (△) 404, (□) 4044 and (◇) 12100 mg l^{-1}.

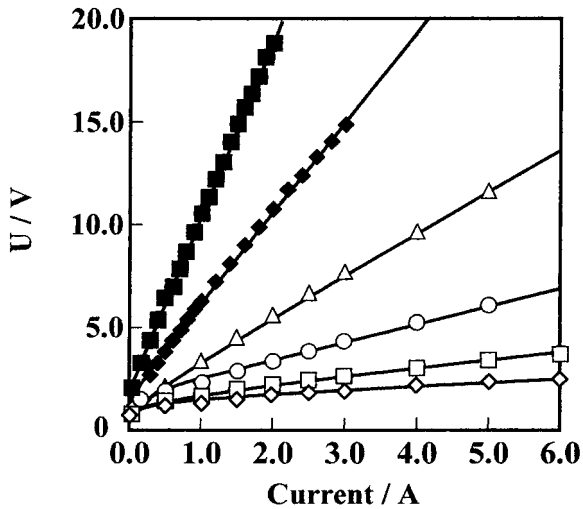

Fig. 7. Influence of chloride ions concentration on current against voltage (U) lines. Condition: [Acetic acid]$_{initial}$ = 4000 mg l^{-1}, V = 150 ml, T = 250 °C and P = 7 MPa. Initially charged gas: 1 MPa oxygen and 2 MPa argon. Chloride ion concentration: (■) 76.0, (◆) 152, (△) 404, (○) 1210, (□) 4044 and (◇) 12 100 mg l^{-1}.

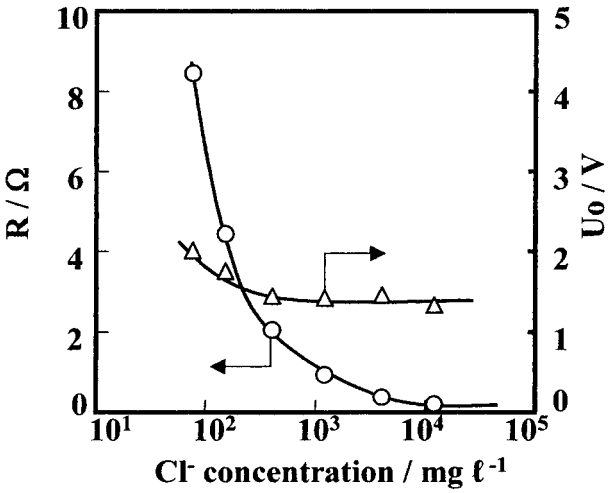

Fig. 8. Electrical resistance between the electrodes and voltage at $i = 0$ A (U_o) calculated by linear regression. Conditions: [Acetic acid]$_{initial}$ = 4000 mg l^{-1}, $V = 150$ ml, $T = 250$ °C and $P = 7$ MPa. Initially charged gas: 1 MPa oxygen and 2 MPa argon.

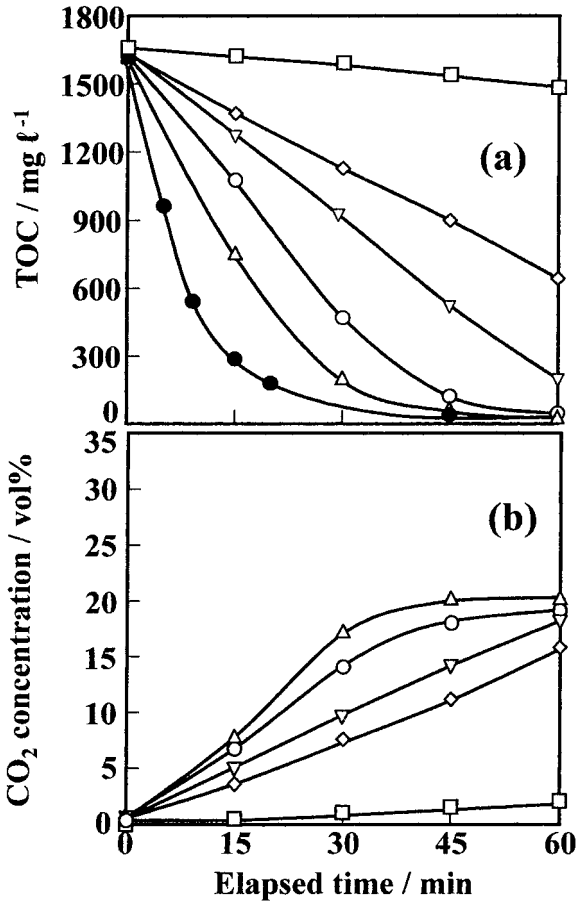

Fig. 9. Influence of electrical current intensity on (a) TOC and (b) CO_2 concentration profile inside autoclave. Conditions: [Acetic acid]$_{initial}$ = 4000 mg l^{-1}, [NaCl] = 2 wt %, $V = 150$ ml, $T = 250$ °C, $P = 7$ MPa. Initially charged gas: 1 MPa oxygen and 2 MPa argon. Current intensity: (□) 0, (◇) 0.5, (▽) 1, (○) 2, (△) 4 and (●) 6 A.

desirable temperature for conducting effective WEO was between 200 °C and 250 °C. The reaction safety aspect also reinforces this minimum desirable temperature. For

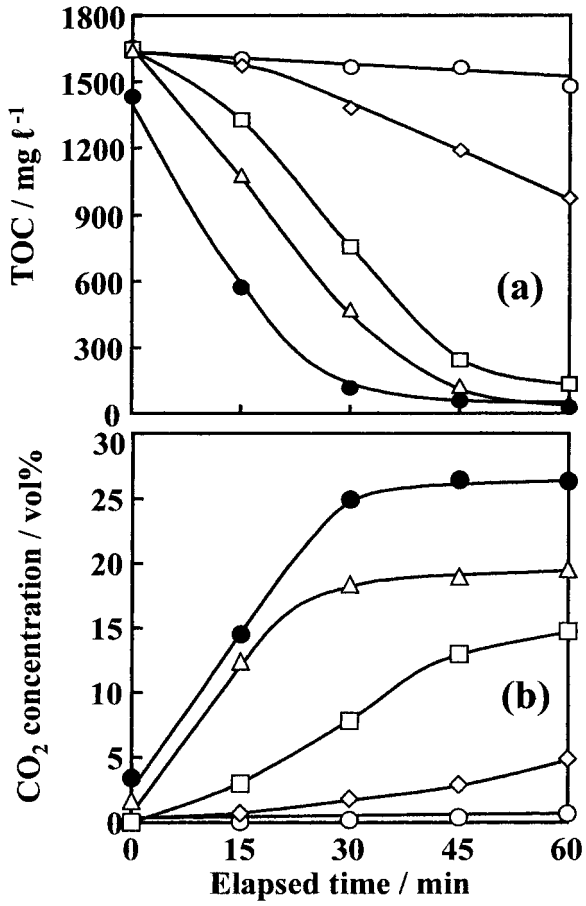

Fig. 10. Influence of temperature on (a) TOC and (b) CO_2 concentration profile inside autoclave. Conditions: [Acetic acid]$_{initial}$ = 4000 mg l^{-1}, [NaCl] = 2 wt %, $V = 150$ ml and $i = 2$ A. Initially charged gas: 1 MPa oxygen and 2 MPa argon. Reaction temperature: (○) 100, (◇) 150, (□) 200, (△) 250 and (●) 300 °C.

WEO conducted at low temperature such as 100 °C, the electrogenerated hydrogen gas concentration inside the autoclave was almost 8 vol % (Figure 11) after charging 2 Ah (the explosion lower limit of hydrogen gas is 4 vol % at room conditions.) Since the autoclave was initially charged with oxygen gas, electrolytic oxidation at a low temperature such as 100 °C means that hydrogen gas will be generated when oxygen gas is present in abundance. A high-temperature/high-pressure reaction is usually synonymous with a hazardous reaction, but in this WEO, we found that keeping the autoclave under high-temperature/high-pressure conditions is safer than keeping it under low-temperature/low-pressure conditions. The increase in temperature to higher than 100 °C enhances the solubility of oxygen gas in liquid water [20]. This may contribute significantly to increasing the efficiency of oxygen gas reduction at the cathode and suppressing the hydrogen evolution.

3.7. *Influence of electrolyte type in WEO*

Aqueous electrolyte solutions with 2 wt % NaOH, Na_2SO_4, KI and KBr were prepared and the catalytic effects of each electrolyte on WEO were investigated.

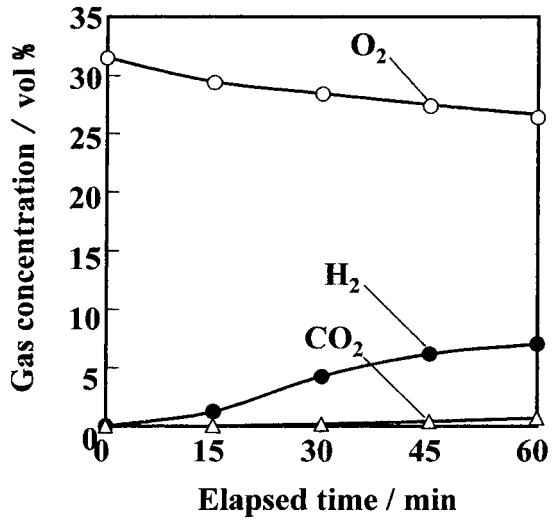

Fig. 11. Gas composition profile inside autoclave for WEO at 100 °C. Conditions: [Acetic acid]$_{initial}$ = 4000 mg l^{-1}, [NaCl] = 2 wt %, V = 150 ml and i = 2 A. Initially charged gas: 1 MPa oxygen and 2 MPa argon.

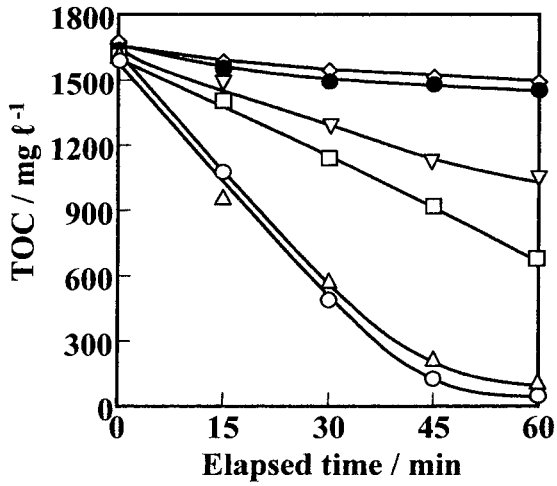

Fig. 12. Influence of electrolyte type on TOC removal profile. Conditions: [Acetic acid]$_{initial}$ = 4000 mg l^{-1}, [Electrolyte] = 2 wt %, V = 150 ml, T = 250 °C, P = 7 MPa, i = 2 A. Initially charged gas: 1 MPa oxygen and 2 MPa argon. Electrolyte type: (◇) deionized water, (●) NaOH, (▽) Na_2SO_4, (□) KI, (△) KBr and (○) NaCl.

The catalytic effects of these salt solutions were compared to those of deionized water and aqueous NaCl solution.

Figure 12 illustrates the TOC removal profile for the different electrolytes. A slow decrease in TOC was observed for WEO runs of acetic acid without salts (deionized water) and with the NaOH electrolyte solution. As discussed previously, the absence of an appropriate catalytic electrolyte seems to influence both anodic and cathodic oxidation. The electrochemical oxidation reaction was strongly influenced by the type of anions present in the solution. For the anions investigated, the catalytic effect on WEO was found to increase in the following order: $OH^- < SO_4^{2-} < I^- \ll Br^- = Cl^-$.

These results suggest that halides have a good catalytic effect in WEO. However, the use of KI as the electrolyte was found not to be favourable because of the red–brown colour in the treated water. This colour was attributed to the anodic oxidation of iodide ions to elemental iodine which seems to be stable under WEO conditions. For all other electrolytes, the final aqueous product was colourless. With regard to the practical application of WEO in wastewater treatment, it was found that chloride salt is the most useful. If the considered wastewater does not contain chloride ions (which is a rare case), seawater, for example, can be added.

3.8. *Comparison between wet oxidation and WEO*

The oxidation capability of WEO was compared with that of wet oxidation in the batch autoclave, by using different organic compounds. Table 1 lists the organic compounds investigated, including phenol, 2-amino-4-chlorophenol, β-naphthol, H-acid, sodium n-dodecilbenzenesulfonate, azophloxine and acetic acid. Table 1 also illustrates the chemical formula and the theoretically required electrical charge (Q^*) of each compound. The organic amounts charged into the autoclave were adjusted for each organic compound to compensate for differences in the theoretically required electrical charge. For the WEO runs, a constant electrical charge of 2 Ah was applied. All wet oxidation and WEO runs were performed in the same autoclave with the platinum anode. For organics with chlorine or sulfur in its molecule, NaOH was initially added to the electrolyte

Table 1. Organic compounds used for comparative runs of WEO with wet oxidation

Organic compound				Amount loaded in 150 ml of 2 wt % NaCl test solution		
Compound	Formula	MW	Q^* /Ah mol^{-1}	Organic amount /m mol	NaOH amount /m mol	Initial pH
Phenol	C_6H_5OH	94.1	750.6	2.85	0	5.0
2-Amino-4-chlorophenol	$NH_2C_6H_3(OH)Cl$	143.6	723.6	2.96	5.1	10.5
β-Naphthol	$C_{10}H_7OH$	144.0	1233.0	1.74	0	4.9
H-acid	$NH_2C_{10}H_4(OH)SO_3NaSO_3H$	341.3	1259.8	1.7	5.1	12.4
Sodium n-dodecilbenzensulfonate	$C_{12}H_{25}C_6H_4SO_3Na$	348.5	2734	0.784	3.8	11.5
Azophloxine	$C_{18}H_{13}N_3Na_2O_8S_2$	509.4	2332	0.92	3.8	11.4
Acetic acid	CH_3COOH	60.0	214.4	10.0	0	2.3

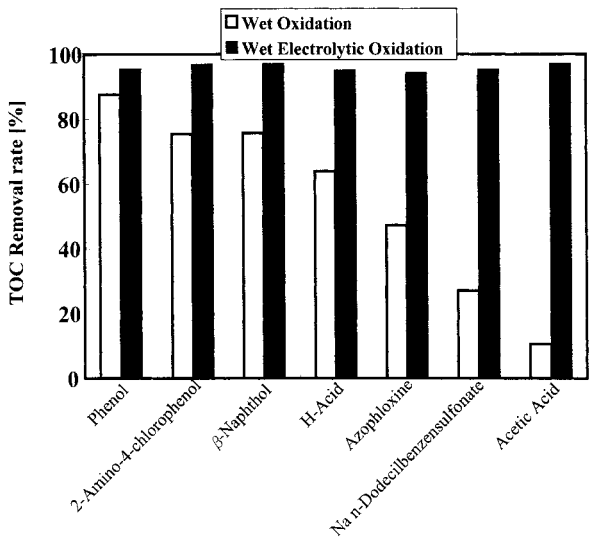

Fig. 13. TOC removal rate performance of WEO and Wet Oxidation for various organics compounds. Conditions: [NaCl] = 2 wt %, V = 150 ml, T = 250 °C, P = 7 MPa, reaction time = 60 min, i = 2 A for WEO runs, i = 0 A for wet oxidation runs. Initially charged gas: 1 MPa oxygen and 2 MPa argon. Other conditions as illustrated in Table 1.

to neutralize the hydrochloric or sulfuric acid resulting from the oxidation reaction.

Figure 13 illustrates the comparative TOC removal rate between wet oxidation and WEO. For all organic compounds tested, the TOC removal rates were better in WEO. Figure 13 also shows that, in wet oxidation, the oxidation rate of organics to mineral compounds such as CO_2 and water is strongly influenced by the chemical stability of each organic compound. On the one hand, organics such as phenol are easily degraded under wet oxidation conditions, but acetic acid is strongly refractory. On the other hand, in WEO, all organics showed almost the same TOC removal rate of over 95% when 2 Ah was supplied to the electrolyte. This WEO performance was not dependent on the initial pH of the aqueous organic electrolyte solution (see Table 1). The resulting treated solutions in phenol, β-naphthol and acetic acid WEO runs (no added NaOH) were slightly acidic because of the presence of carbonic acid formed by CO_2 dissolution in water. Furthermore, initial electrolyte solutions of β-naphthol, H-acid and azophloxine, which are chemicals used in dye manufacturing, were strongly coloured but after the WEO treatment, they became completely colourless.

4. Conclusions

Despite the uncertainties remaining concerning the oxidation mechanism, differences in the governing reactions of WEO with low-temperature electrolysis were clearly revealed. Electrolysis of aqueous NaCl solution under high-temperature/high-pressure conditions greatly suppressed oxygen gas, hydrogen gas and free residual chlorine evolution. Halide ions such as chloride ions were recognized to work as catalysts and their presence was found to be essential for achieving effective TOC removal in WEO. The addition of external oxygen in WEO of acetic acid allowed us to achieve an apparent current efficiency higher than 100%, when acetic acid was present in abundance. This was found to be due to the progress of the electrochemical conversion of oxygen gas to active oxygen, in place of hydrogen evolution, at the cathode. The oxidation rate of organics in WEO was mainly controlled by the amount of supplied electrical charge.

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