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Electrochemical oxidation in pigment wastewater treatment using a Ti/IrO$_2$ tube-type electrode

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ABSTRACT

The objectives of this study are to investigate characteristics of electrochemical oxidation of wastewater depending on electrode materials and to analyze the influence of the chloride ion as an electrolyte on electrochemical oxidation of pigment wastewater using a Ti/IrO$_2$ tube-type electrode. The Ti/IrO$_2$ electrode was adopted as the most proper material in the comparative analysis under COD removal efficiency and current efficiency. The current efficiency for each electrode material was decreased in the order of Ti/IrO$_2$ 16.5%, Ti/Pt 14.0%, and graphite 3.4%. Two kinds of electrolytes of NaCl and Na$_2$SO$_4$ revealed different levels of electrochemical oxidation under the same conductivity conditions. Specific energy consumption was reduced by adding a chloride ion in the electrochemical oxidation treatment. The chlorite ion (ClO_2^-) and free chlorine were produced in the Ti/IrO$_2$ tube-type electrochemical oxidation systems. The production amount of chlorite ion was larger than double that of free chlorine production. The indirect oxidation process by the intermediate product was concluded to be the major principle for COD removal.

Keywords: Chloride ion; Electrochemical oxidation; Electrolyte; Pigment wastewater; Ti/IrO$_2$; Tube-type electrode

1. Introduction

Advanced wastewater treatment technology is an important theme for environmental scientists and engineers. The electrochemical oxidation process for industrial wastewater treatment is recognized to be applicable due to the high organic removal and fast reaction time without relation to the pollutant biodegradability [1–3]. However, electrochemical treatment characteristics widely vary according to the reactor type, electrode material, pollutant matter, wastewater conductivity, etc. [4–6].

Electrochemical oxidation devices have been continuously developed since the prototype invention in the early 20th century. Among the electrode types, the plate type and rod type were widely used for practical applications [4,6]. The tube-type electrode was adopted in this research. The tube-type electrode was expected to be proper for the management and replacement of electrodes and for the maximum oxidation effect through the water flow between the anode and the cathode [7]. To obtain a high pollutant removal rate and economic feasibility, the selection of proper electrode material is important [7–14]. The characteristics of each electrode material shows variable electrocatalytic function and different removal rate of pollutants [4,13].

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Electrode materials of titanium electroplated with IrO_2, titanium electroplated with platinum, and graphite were used in this research for the tube type electrolysis reactor. The evaluation of electrode material was conducted through the variation of COD removal efficiency and current efficiency. The effect of chloride concentration was investigated comparing electrolyte matter, production of chlorite and free chlorine, and specific energy consumption. The electrochemical oxidation characteristics of refractory pigment wastewater were evaluated with removal rate of chemical oxygen demand.

2. Materials and methods

2.1. Characteristics of wastewaters

The characteristics of pigment wastewater used in the experiment are shown in Table 1. Pigment wastewater effluent from the U Chemical company, which produces organic pigment, inorganic pigment, and fluorescent pigment, was supplied for electrochemical treatment. The effluent was made through the chemical coagulation and flotation process with polyelectrolytes, and secondary biological treatment and sedimentation. Synthetic domestic sewage was prepared with the food waste from the K University cafeteria. The food waste was processed and filtered with a sieve, which was stored in the refrigerator.

The pigment wastewater showed low biodegradability and high electrolyte concentration with 150–400 mgCOD/L and 1,200–2,000 mgCl^-/L. The synthetic domestic sewage had 12–16mg Cl^-/L and low conductivity of 0.03–0.04 mhos/m. The organic concentration was controlled with glucose ($C_6H_{12}O_6$). NaCl was provided to control the conductivity and the chloride ion concentration was set to 1,000, 1,500, 2,000 and 2,500 mg/L.

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Table 1
Characteristics of wastewaters used for the experiment

Items	Pigment wastewater		Synthetic domestic sewage	
	Range	Average	Range	Average
pH	6.0–8.5	7.3	6.8–7.2	7.0
COD (mg/L)	150–400	275	200	200
Cl^- (mg/L)	1,200–2,000	1,600	12–16	14
Conductivity (mhos/m)	0.58–1.30	0.94	0.03–0.04	0.035

2.2. Experimental apparatus

The photo of tube-type electrolysis apparatus is shown in Fig. 1. The apparatus consists of a power supplier, a peristaltic pump, tube type electrodes, and bus bar. The maximum flow rate of the pump was 1.7 L/min, and capacity of power supplier was 3.8 kW. The electrode used to experiment the effect of chloride ion and electrode materials consists of a tube-type cathode and rod-type anode, which provide a concentrical surface of electrodes. The diameters of the inner surface of the cathodes were 21.4 mm and 35.7 mm, respectively. The diameter of the outer surface of the rod was 16.0 mm. The distance between the anode and cathode was 2.7 mm, and 9.85 mm respectively and the effective length of electrodes was 300 mm.

The wastewater was fed to the tube-type electrode by a peristaltic pump. In order to obtain the electrochemical oxidation reaction, direct current from the power supplier was applied to the wastewater between the anode and the cathode. For the electrochemical oxidation apparatus, electrodes were connected in series and five electrodes could be used at maximum capacity. The kinds of insoluble anode materials used in the experiment were titanium electrically coated with IrO_2, titanium electrically coated with platinum, and graphite. Cathode material was stainless steel for all cases.

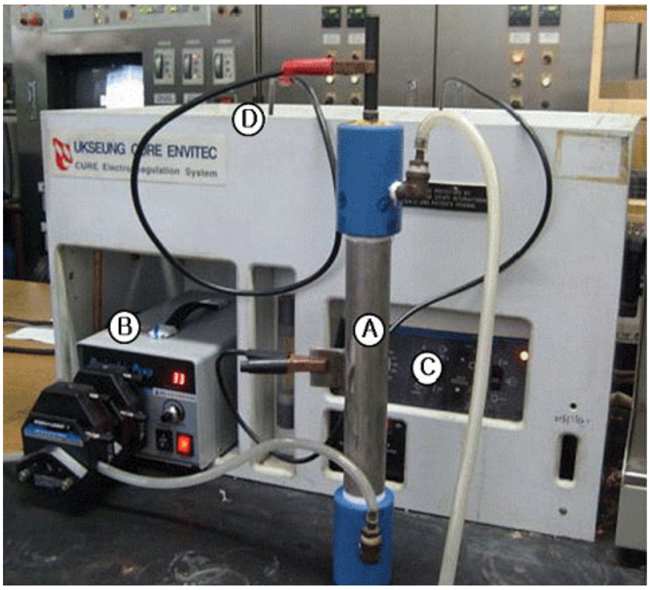

Fig. 1. Photo of tube-type electrolysis apparatus. A, tube-type electrode. B, peristaltic pump. C, power supplier. D, bus bar.

2.3. Experimental methods

Current efficiency on the electrode material was evaluated through analyzing COD removal of pigment wastewater for each electrode material. The current value was 10 A in the experiment which was calculated to 6.7 A/dm^2 in current density.

To compare electrolyte effects, NaCl and Na_2SO_4 were used to obtain the conductivity of 0.6 mhos/m. Glucose was dosed for the synthetic wastewater as organic source. COD removal rate and conductivity variation were measured during the electrolysis experiment. Production of chlorite ions and free chlorine were also measured for the glucose solution. The current density of 6.7 A/dm^2 was applied to the electrolysis experiment and the hydraulic retention time was controlled in the range of 56–168 s.

Specific energy consumption was evaluated under the chloride concentration of 1,000, 1,500, 2,000 and 2,500 mg/L. The conductivity was respectively 0.34, 0.49, 0.60 and 0.76 mhos/m. The current density of 6.7 A/dm^2 was applied for the electrolysis and the hydraulic retention time in the electrode tube was controlled to 18 s.

Parameters focused in this research were pH, COD, conductivity, chloride, chlorite, chlorate and free chlorine. Analysis methods followed the Standard Methods. Chloride was measured through silver nitrate titrimetric method and free chlorine was analyzed through the N,N-diethyl-p-phenylenediamine ferrous titrametric method.

Chlorite ion and chlorate ion were analyzed with a Waters 600 ion chromatograph with a Waters 432 conductivity detector. Column was IC-Pak Anion HR and detection sensitivity was maximized by removing anions in solution with the Alltech 335 SPCS suppressor. 10 mM NaOH was used as eluant whose flow rate was 0.8 mL/min. Standard solutions of chlorite and chlorate were prepared with $NaClO_2$ and $NaClO_3$ respectively. The retention time for chlorite peak and chlorate peak was 3.465 min and 4.857 min respectively. Sample injection volume for ion chromatography was 50 μL, which was pretreated with a membrane filter.

3. Results and discussion

3.1. Selection of electrode materials

3.1.1. Relationship between voltage and current density

The relationships between voltage and current density are illustrated in Fig. 2 for each electrode material. The increase of voltage showed a linear relationship with current density at each condition of electrode materials and electrolytes. When the high concentration of electrolyte was applied, a steep slope is seen in the graph of voltage vs. current density. As the high electrolyte concentration results in high conductivity, high current density can be obtained at low voltage condition that will save electricity consumption.

The voltage of current density 6.0 A/dm^2 was 4.6 V for Ti/IrO_2, 4,8 V for Ti/Pt, 5.0 V for graphite respectively at the electrolyte concentration of NaCl 0.14 M. As the lowest voltage was obtained from the electrolysis using the Ti/IrO_2 electrode, Ti/IrO_2 electrode had the highest electrolysis efficiency for the preliminary electrolysis process. This means that Ti/IrO_2 electrodes will reveal higher current density than the Ti/Pt electrode or graphite electrode when the electrolysis is operated under the same voltage condition. From the slope increase of the linear equation for current density vs. voltage, high conductivity condition was expected to make stable voltage conditions which were necessary for preventing electrical shocks on systems. The graphite electrode reached hot temperature

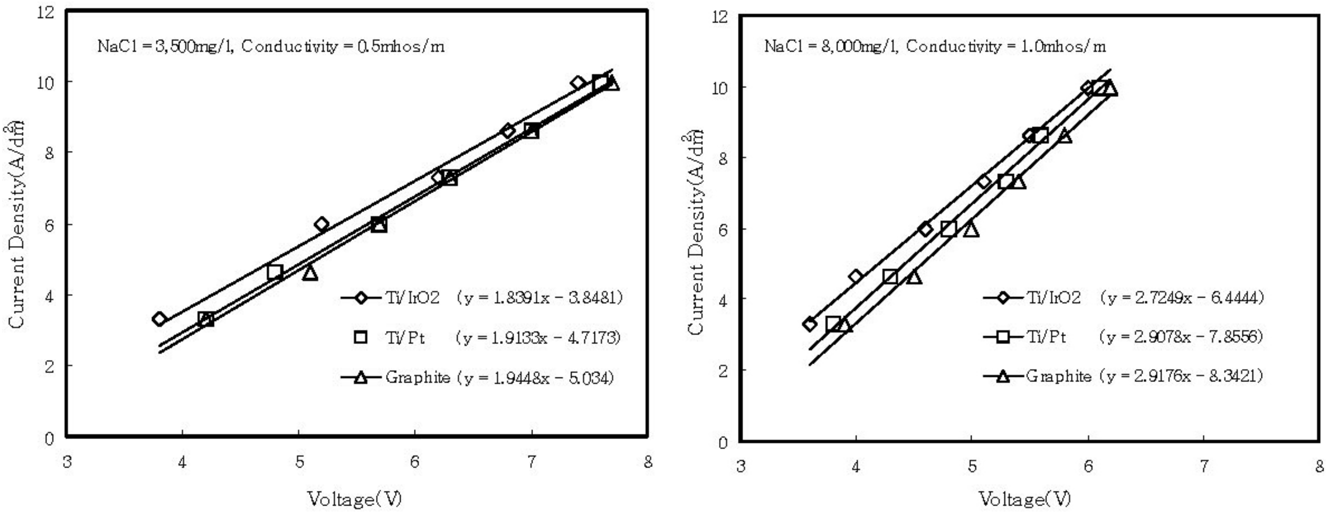

Fig. 2. Current density vs. voltage depending on electrode materials at NaCl = 3,500 mg/L and NaCl = 8,000 mg/L.

as the current density increases. The surface of graphite electrode was observed to have weak strength at hot surface temperature condition.

3.1.2. Current efficiency

For comparing electrode material effects among Ti/IrO_2, Ti/Pt and graphite, results of current efficiency and COD removal efficiency are shown in Table 2 while the electrolysis was conducted for the pigment wastewater with the hydraulic retention time of 12 and 24 s. The Ti/IrO_2 electrode was observed to be the most proper for all conditions as it showed higher current efficiency and COD removal efficiency than that of other electrode materials. On Ti/IrO_2 electrode, current efficiency and COD removal efficiency were 78.2% and 16.5% for hydraulic retention time of 12 s. For an hydraulic retention time of 24 s, current efficiency and COD removal efficiency were 93.3% and 9.9%. But the graphite and Ti/Pt electrodes showed relatively low current efficiency and COD removal efficiency for the retention time of 12 and 24 s. The titanium electrode electroplated with iridium dioxide, Ti/IrO_2, improved electrocatalytic characteristics for the current efficiency and COD removal efficiency in electrolysis process in comparison to the graphite and Ti/Pt electrodes.

Important factors for selecting electrode materials are generally electrocatalytic characteristics, electrode stability and conductivity, in addition to the physical and thermal stability, current efficiency and COD removal efficiency. The feasibility order for practical use was evaluated to be down order of Ti/IrO_2, Ti/Pt, and graphite from the viewpoint of above factors.

3.2. Influences of chloride ion

3.2.1. Effect of electrolyte

On the electrochemical oxidation process of the pollutants, the reaction mechanism was investigated through the COD removal comparison according to the different electrolyte. The material of the electrode was Ti/IrO_2 which was recognized to be proper for the high electrolysis efficiency. When current density was 6.7 A/dm^2, COD concentration and conductivity variation are illustrated in Fig. 3 according to NaCl and Na_2SO_4 electrolytes.

Table 2
COD removal efficiency variation depending on electrode materials (Influent COD = 300.4 mg/L)

Electrode materials	Retention time (s)	Effluent COD conc. (mg/L)	COD removal efficiency (%)	Current efficiency (%)
Ti/IrO_2	12	65.5	78.2	16.5
	24	20.0	93.3	9.9
Ti/Pt	12	101.8	66.1	14.0
	24	73.7	75.5	8.0
Graphite	12	252.0	16.1	3.4
	24	248.0	17.4	1.8

When NaCl was dosed as an electrolyte, COD concentration was decreased according to the retention time. But when Na_2SO_4 was dosed as an electrolyte, COD variation was small. This means the chloride ion has an important role in the electrochemical oxidation process [15–17].

While NaCl was dosed as electrolyte, the COD concentration of feed wastewater was 540 mg/L and the COD concentration was decreased to 100 mg/L during the retention time of 24 s. The COD removal efficiency of this case was 81.5%. When Na_2SO_4 was dosed as an electrolyte, the COD concentration of feed wastewater was 416 mg/L and the COD concentration was decreased to 364 mg/L during the retention time of 24 s. The COD removal rate of this case was 12.5%. The conductivity variation according to the retention time was measured during the electrolysis experiment. When NaCl was dosed as electrolyte, the conductivity was decreased according to the retention time. But when Na_2SO_4 was dosed as the electrolyte, the conductivity varied little. This observation was thought to mean that the conductivity decrease has a relation to the production of chlorine from chloride ion in electrolysis process. The conductivity of feed wastewater showed 0.633 mhos/m, but that of treated water decreased to 0.523 mhos/m at the retention time of 24 s.

Variation of COD, chloride concentration and ratio of $\Delta COD/\Delta Cl^-$ with retention time are shown in Table 3 while the electrolysis process was operated with NaCl electrolyte and current density of 6.7 A/dm^2. From the results, the COD concentration decreased in proportion to the chloride ion consumption according to retention time. The COD concentrations of feed wastewater and treated

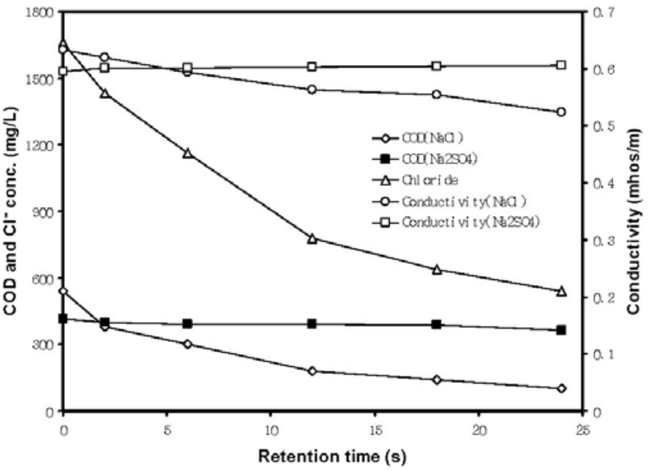

Fig. 3. Effects of electrolytes on the COD concentration and conductivity.

Table 3
COD removal ratios per unit mass consumption of Cl^- in electrolysis process

Items	Retention time, s					
	0	2	6	12	18	24
COD (mg/L)	540	380	300	180	140	100
Cl^- (mg/L)	1,659	1,432	1,163	780	638	539
$\Delta COD/\Delta Cl^-$	—	0.70	0.47	0.31	0.28	0.40

water were 540 mg/L and 100 mg/L respectively at the retention time of 24 s. At this case, the chloride ion concentrations of feed wastewater and treated water were 1,659 mg/L and 539 mg/L respectively.

On the other hand, the COD removal per unit mass consumption of chloride ion, $\Delta COD/\Delta Cl^-$ was calculated. The ratio of $\Delta COD/\Delta Cl^-$ has the range of 0.28–0.70 and the average value of 0.39 mgCOD/mgCl^-. Therefore when NaCl was dosed as electrolyte, decrease of COD concentration and conductivity was observed to have relation with chloride ion consumption in electrolysis process.

3.2.2. Production of chlorite ion and free chlorine

Production of the chlorite ion and free chlorine were investigated in order to identify the oxidizing intermediate product which has indirect oxidation effects in the electrolysis of wastewater containing chloride ion. Synthetic wastewater was made of glucose as organic source and distilled water, and chloride ion was supplied with NaCl.

In Fig. 4, chlorine compounds including chloride ion and COD concentration variation were illustrated according to retention time. When retention time was increased, chloride ion and COD concentration were decreased, but chlorite, ClO_2^- and free chlorine concentration increased [6]. The chlorate ion, ClO_3^-, was not detected in the electrolysis process.

When the influent COD concentration was 400 mg/L in the electrolysis experiment, the effluent COD concentration was 210 mg/L in the retention time of 168 s and the COD removal rate was 47.5%. In this experiment, the chloride ion concentrations of influent and effluent were 1,546 mg/L and 1,049 mg/L respectively, which showed a concentration drop of 496 mg/L for the retention time of 168 s. At the same time, chlorite and free chlorine concentration were increased from null to 261 mg/L and 82 mg/L respectively.

From the mass balance of the consumed chloride in electrolysis process, the chlorine compounds and chlorine gas production were calculated and illustrated in Fig.5. Production amount of chlorite, chlorate and free chlorine were relatively small and large proportion of consumed chloride was estimated to have conversion into the other type chlorine compounds and chlorine gas. After the retention time of 112 s, the consumption of chloride approached the upper limit, but the production of free chlorine and chlorite was observed to increase continuously in the electrolysis reaction.

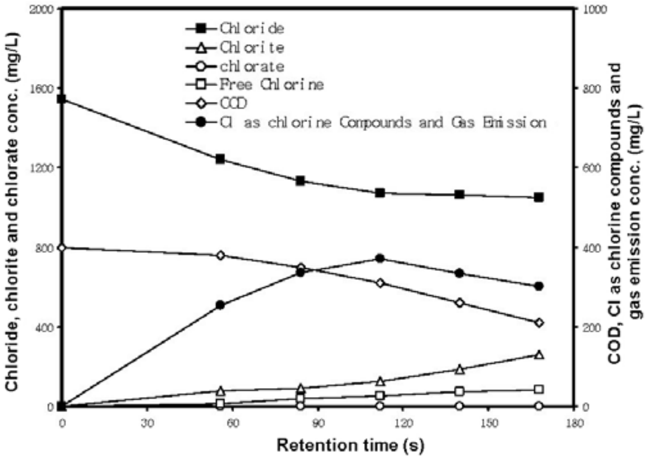

Fig. 4. Variations of chlorine compounds and COD concentration according to retention time.

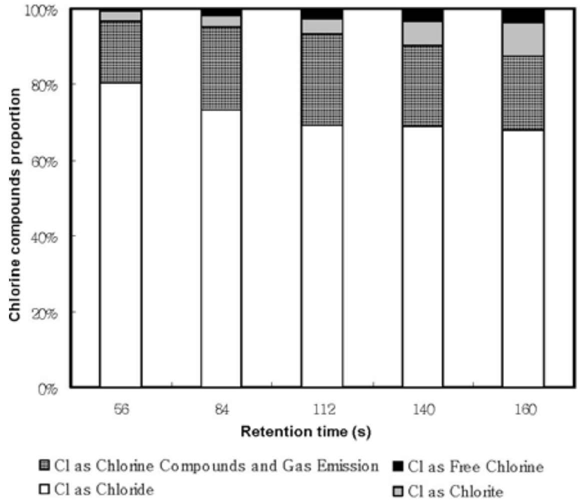

Fig. 5. Mass balance of chlorine compounds according to retention time.

The indirect oxidation through the intermediate product of chlorite and free chlorine was speculated in electrolysis experiment. Chlorite was generally known to be a more effective oxidant than free chlorine. According to the retention time in the electrolysis process, the production of chlorite increased more than twice that of free chlorine. The production of chlorite was found to be a major factor in the electrochemical oxidation process.

The production of chlorite ion was concluded to be one of major factors for the electrochemical oxidation of organics as the large amount of chloride in influent was converted to chlorite rather than free chlorine in the

Table 4
Chloride effects on specific energy consumption and current efficiency

Chloride concentration (mg/L)	1,000	1,500	2,000	2,500
Influent COD concentration (mg/L)	200	200	200	200
Effluent COD concentration (mg/L)	60	40	10	0
COD removal efficiency (%)	70	80	95	100
Current efficiency (%)	6.6	7.5	8.9	9.4
Specific energy consumption (kWh/gCOD)	0.44	0.34	0.28	0.24

electrolysis process. Therefore, studies of the devices and operation conditions of electrolysis process are needed in future to improve electrochemical oxidation efficiency [5].

3.2.3. Specific energy consumption

Electrochemical treatment was conducted for domestic sewage with the Ti/IrO$_2$ electrode, current density of 6.7 A/dm^2 and retention time of 18 s, COD removal efficiency and variation of specific energy consumption; the results are summarized in Table 4. While chloride ion concentration was controlled in the range of 1,000–2,500 mg/L, the conductivity was detected in 0.34–0.76 mhos/m. According to the increase of chloride ion concentration, the COD removal efficiency was improved but specific energy consumption rate was decreased. At an influent chloride concentration of 1,000 mg/L, the COD removal efficiency and specific energy consumption were 70% and 0.44 kWh/gCOD respectively. And at the influent chloride concentration of 2,500 mg/L, COD removal efficiency and specific energy consumption were 100% and 0.24 kWh/gCOD respectively.

An indirect oxidation reaction was thought to occur with the Cl_2 and $HOCl/OCl^-$ produced in the electrolysis process. An improvement of the specific energy consumption rate was revealed as the chloride ion concentration increased. Therefore, effective COD removal and reaction energy reduction could be obtained when the proper conductivity of influent could be maintained with chloride ion dose in electrolysis process.

4. Conclusions

Electrochemical oxidation of refractory industrial wastewater was investigated in this research. Electrode materials of titanium electroplated with iridium dioxide, titanium electroplated with platinum, and graphite were used for the tube type electrolysis reactor. The evaluation of electrode material was conducted through the variation of current density and COD removal efficiency. The electrochemical oxidation characteristics of refractory pigment wastewater were evaluated and obtained conclusions are as follows:

1. When a high concentration of electrolyte was applied, a steep slope was seen in the graph of voltage vs. current density. As a high electrolyte concentration results in high conductivity, high current density can be obtained at low voltage conditions that will save electricity consumption. As the lowest voltage was obtained from the electrolysis using the Ti/IrO$_2$ electrode, it had the highest electrolysis efficiency for the preliminary electrolysis process.
2. The Ti/IrO$_2$ electrode was adopted as the most appropriate material in the comparative analysis under COD removal efficiency and current efficiency. Current efficiency for each electrode material decreased in the order of Ti/IrO$_2$ 16.5%, Ti/Pt 14.0%, and graphite 3.4%.
3. When NaCl was dosed as the electrolyte, COD removal efficiency was 81.5% at the retention time of 24 s. But when Na_2SO_4 was dosed as the electrolyte, COD removal efficiency was low, which means that the chloride ion has an important role in the electrochemical oxidation process.
4. When NaCl was dosed as the electrolyte, COD concentration decreased according to retention time, and chloride ion concentration and conductivity also decreased at the same time. The COD removal per unit mass consumption of chloride ion, $\Delta COD/\Delta Cl^-$, was calculated. The ratio of $\Delta COD/\Delta Cl^-$ has been observed in the range of 0.28–0.70 mgCOD/mgCl$^-$ and an average value of 0.39 mgCOD/mgCl$^-$.
5. The indirect oxidation through the intermediate product of chlorite ion and free chlorine was hypothesized in the electrolysis experiment. The chlorite ion was generally known to be a more effective oxidant than free chlorine. According to the retention time in the electrolysis process, the production of chlorite ion increased more than twice that free chlorine production. The production of chlorite was found to be a major factor in the electrochemical oxidation process.
6. The specific energy consumption rate decreased according to the increase of the influent chloride concentration. When the influent chloride concentration was 2,500 mg/L, the specific energy consumption rate was 0.24 kWh/gCOD. Effective COD removal and reduction of energy consumption could be obtained when the proper conductivity of influent was maintained with chloride dose in electrolysis process.

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