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Effect of general ions on biological treatment of perchlorates in smelting wastewater

Shin-Jo Kim*, Ki-Yong Lee, Ki-Cheol Lee, Namil Chung, Dong-Il Jung

Han-river Environmental Research Center, National Institute of Environmental Research
627 Yangsu-ri, Yangseo-myeon, Yangpyeong-kun, Kyounggi Province 476-823, Republic of Korea
Tel. +82 31 770 7250; Fax: +82 31 773 2268; email: sjkim1212@korea.kr

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ABSTRACT

The objective of this work was to investigate SO_4^{2-}-, Cl^--, and CO_3^{2-}- ions interference on the effectiveness of perchlorate removal from smelting wastewaters in order to select adaptive biotechnological solutions. Ion chromatography using the EPA method 314.0 was utilized for the perchlorate determination. The precision, the method detection limits (MDL), and the minimum reporting level (MRL) of the analytical method were critically examined. In spite of the strong inhibitory effects of the dissolved inorganic substances contained in smelting wastewater, microbes could cope with their relatively high concentration allowing the subsequent biological treatment to reduce effectively the perchlorates concentration to a satisfactory level. The increase of the SO_4^{2-}-concentration from 0 to 16,000 ppm (conductivity: 428 → 24,800 μS/cm) led to a reduction of the perchlorates biodegradation rate by approximately 10 times from 0.0365/h to 0.0033/h. However, most of the perchlorates were removed after a hydraulic retention time (HRT) of half a day with mixed liquor volatile suspended solid (MLVSS) of 2000–3000 ppm. The introduction to the bioreactor of influent containing a SO_4^{2-}-concentration of 20,000 ppm (conductivity: 30,100 μS/cm) resulted in almost complete removal of perchlorates below the detection limit for a short period of time. The persistence of this condition, however, seriously inhibited the microbial activity.

Keywords: Perchlorate; Zinc smelting; Conductivity; Biological treatment; Percent difference; Distortion

1. Introduction

Since their first successful artificial synthesis in the 1890s in Sweden, perchlorates (ClO_4^-) have been extensively applied as propellant for rockets and missiles, commercial explosive, air bag initiator in vehicles, fire work gunpowder, reagents, etc [1]. The perchlorate ion has the tetrahedral structure with four oxygen atoms surrounding the chlorine atom. The high oxygen contents of perchlorate salts make them ideal as oxidizers.

The perchlorates released to the environment, being soluble in water, are introduced to the aqueous systems and move rather long distance from the source through the aquatic paths. They do not form covalent bonds with other ions, and linger in the environment. Perchlorates are easily introduced to the human body through the polluted food and water. Perchlorates, although used for medical purposes, react with the sodium iodine symporter and inhibit the iodine uptake by thyroid, causing hypothyroidism and subsequently affect the thyroid hormone secretion [2]. The insufficient release of these hormones

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*Corresponding author.

can cause problems in development of conspectuses or the growth of infants such as an irreversible brain damage [3]. The insufficient intake of iodine can also induce thyroid functional disorder in pregnant or breast-feeding women followed by developmental disability or learning disorder in fetus or infants. The daily oral exposure (reference dose, RfD) to perchlorates of a normal person is 0.7 μg/kg/day, the amount that is not likely to cause harmful effects during his lifetime. The United States Environmental Protection Agency (US EPA) had set the drinking water equivalent level (DWEL) of perchlorates to 24.5 ppb (ppb) and reduced it to 15.0 ppb (ppb) in 2008. In Massachusetts and California, the compulsory standard was set to 2 and 6 ppb, respectively, and in other states, in the range of 4–51 ppb [4].

Thus, it is crucial to maintain the amount of the perchlorates in the environment up to a point; the challenges have been focused on how to eliminate waste materials efficiently. The purification of the ground/drinking water can be achieved by means of simple ion exchange systems, whereas for the treatment of wastewaters containing high concentrations of dissolved inorganic substances, heavy-duty ion exchange processes, membrane separations (i.e. electrodialysis and reverse osmosis) or electrochemical reduction using zero-valent iron are necessary [8]. However, the industrial-scale purification of perchlorates containing wastewaters from LCD plants, chemical factories and smelting industries cannot be stably performed by conventional physicochemical treatment methods.

Recently, researchers reported the removal of perchlorates from organic wastewaters using a biological treatment by anaerobic/aerobic reactions [5]. Microorganisms prefer NO_3^-, NO_2^- or ClO_3^- as electron accept ors to perchlorates under anaerobic condition [6]. Thus, it is possible to induce the growth of microorganisms by allowing the degradation of the perchlorates through addition of the electron acceptors such as NO_3^-, NO_2^- or ClO_3^- into the wastewater. In addition, a biological treatment scheme with these characteristics will be useful to remove perchlorates from wastewaters containing high concentrations of total dissolved solids. Ions inhibit microbial growth and activity which degrade perchlorates in the wastewater [7].

This research proposes an effective biological treatment of perchlorates in smelting wastewaters containing high concentration of total dissolved solids after the dilution of the toxic material and addition of carbon source. The experimental work was carried out using the wastewater discharged from a factory with the biological treatment unit devised through the examination of wastewater characteristics and reduction technology.

2. Experiment and analysis

2.1. Experimental method

The biological treatment experiments included both batch and continuous reactors. The experiments using a batch reactor was carried out by mixing wastewater treated, acetic acid, nutrients and sludge for 6–8 h. The wastewater was obtained from the effluent of the selective zinc precipitation (SZP) process of zinc smelting and was diluted with distilled water to adjust the concentrations of SO_4^{2-} to 0, 8000, 12,000, 16,000 and 20,000 ppm. To maintain the concentration of perchlorates unchanged before and after the dilution of wastewater, $NaClO_4$ was added to the reactor. The final concentration of acetic acid added as the extraneous carbon source was 150 ppm. As additional nutrients, urea was added to set the level of ammonium nitrogen to 25 ppm and KH_2PO_4 and K_2HPO_4 were used to set the level of phosphorus to 25 ppm. The level of $MgSO_4$ was set to 2 ppm and the level of yeast extract was set to 25 ppm (dry weight). The microorganisms for perchlorate degradation were obtained from the return sludge from a sewage treatment plant and acclimated to the experimental condition. In the experiment without smelting wastewater (i.e., 0 ppm SO_4^{2-}), the inoculums sludge was acclimated to the same culture solution for 7 days.

In the experiment using the smelting wastewater, the microorganisms were cultivated under the condition of increasing concentration of total dissolved solids, gradually decreasing the dilution factor of the wastewater for 6 days before adjusting the concentration of SO_4^{2-} to the target concentration 1 day prior to the experiment. The acclimation of microorganisms to the target sulfate concentration was allowed for 5 days in the follow-up batch reactor experiments. The sludge was washed three times with cultivation solution and inoculated to the reactor in the amount of MLVSS to reach 650 ppm, which was increased to 1500 ppm in the follow-up experiments. After mixing, the sludge was aerated with pure nitrogen gas for 5 min to eliminate dissolved oxygen. The reactor was sealed with a cap after pH was adjusted to 7.0 and the sludge was aerated with nitrogen gas for additional 2 min. The reactor, whose concentration was 0 ppm, was monitored in the absence of SO_4^{2-} using a pH meter through the hole in the sealing cap. Every reactor was stirred completely through the experimental processes.

The experimental system for the continuous reactor experiment was composed of anaerobic and aerobic reactors and a precipitation tank (Fig. 1) whose retention times were set to 0.5, 0.2 and 0.8 day, respectively. A stirring apparatus was installed in the anaerobic reactor for mixing, and an aerator was equipped for mixing and oxygen supply. The wastewater used in the experiments was supplied by the Smelting Factory A and diluted

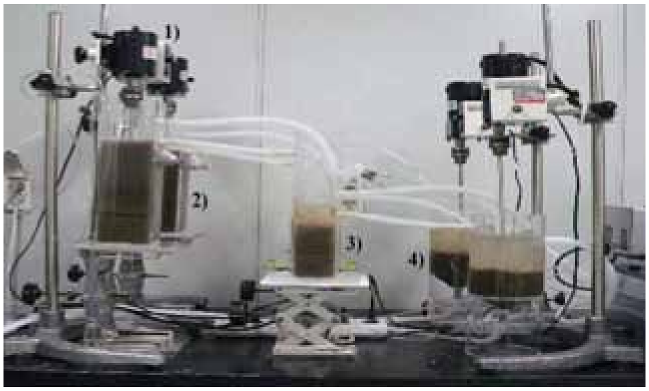

Fig. 1. The biological reactors for the continuous perchlorate treatment experiment. (1) Rotating motor, and various reactors of (2) anaerobic/anoxic (3) aerobic and (4) settling.

with tap water before the experiments. Each of four bioreactors received diluted wastewater, whose SO_4^{2-} concentration was different from one another (<500–25,000 ppm) with a rate of 2 L/d. As exogenous carbon source, acetic acid (300 ppm), nitrogen (15 ppm, urea was used) and phosphorus (5 ppm) were added to the diluted wastewater, and pH was set to 5.0 before the wastewater was introduced into the reactors in order to keep their pH neutral. For the microbial inoculation, the return sludge from the biological treatment facility of Smelting Factory A and the sewage treatment plant were mixed. The amount of MLVSS in the anaerobic reactors ranged between 2000 and 3000 ppm.

2.2. Analytical methods

The analysis of perchlorates was performed according to the EPA method 314.0 [7]. The concentration of perchlorates was determined by ion chromatography (IC; DX500, Dionex) using AG16/AS16 and AG20/AS20 columns. The IC conditions for the perchlorate analysis are summarized in Table 1. In this study, 1 mL samples were introduced into the IC system that comprised of a pump, injection valve, guard column, analytical column, suppressor, and conductivity detector.

Before the perchlorate analysis, we evaluated the accuracy of the chromatographic columns (AG16/AS16 and AG20/AS20) used for the analysis of perchlorates. The method detection limit (MDL), the detectable minimum concentration, and the minimum reporting level (MRL), the quantifiable minimum concentration of perchlorates, were compared.

The precision of analysis, the detection limits and the effect of interfering ions (SO_4^{2-}, Cl^-, CO_3^{2-}) were also considered in the evaluation of the results. Deionized water was used for all the analyses, and the samples were filtered through 0.45 μm filters.

Table 1
IC condition for perchlorate analysis

IC	DX500 (Dionex)
Column	AG16 (4 mm, Dionex), AS16 (4 mm, Dionex)
	AG20 (4 mm, Dionex), AS20 (4 mm, Dionex)
Suppressor	ULTRAII ASRS 4 mm (300 mA, Dionex)
Detector	ED40 (Dionex)
Injection volume	1000 μL
Eluent	50 mM NaOH
Flow rate	1.0 mL/min for AS16 and 1.2 mL/min for AS20

To investigate the effect of anion interference, a mixed solution of NaCl, Na_2SO_4 and Na_2CO_3 containing 5000 ppm of the individual anions (SO_4^{2-}, Cl^- and CO_3^{2-}) was prepared. The mixed solution was diluted to prepare sample solutions with anion concentration ranging 0–1000 ppm. Twenty five ppb perchlorates were added to the sample solutions.

The perchlorate recovery rate was determined using diluted (5×) and un-diluted smelting wastewater, into which perchlorates (10 ppb) were added. Perchlorates in both samples were measured with five replicates, and the recovery rate was determined by subtracting the concentration of perchlorates in the diluted blank samples (no addition of perchlorates) from the corresponding value of the samples with added perchlorates.

3. Results and discussion

3.1. Determination of MDL and MRL

The results obtained by the AG16/AS16 column for the solutions containing 5 and 10 ppb were 1.2 and 1.6 ppb, respectively. The corresponding values obtained using the AG20/AS20 column were rather similar (1.1 and 1.2 ppb, respectively).

In general, the MRL for perchlorates is three times higher than the MDL or five times higher than the noise in the chromatogram [9]. The values of three times MDL for the sample concentrations of 5 and 10 ppb were 3.5 and 4.7 ppb with AG16/AS16 column and 3.3 and 3.5 ppb with AG20/AS20 column, respectively. Considering the noise of the chromatogram, the MRL for perchlorates should be greater than the values above.

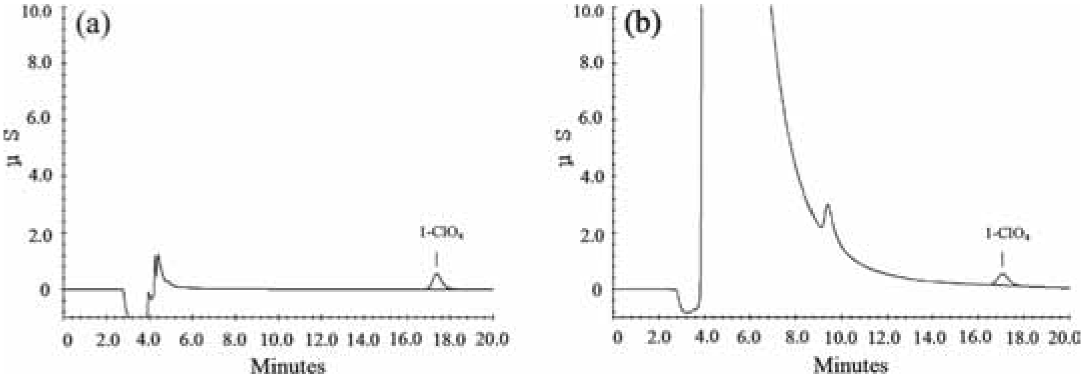

Fig. 2. The chromatogram for the samples containing 25 ppb perchlorate (a) without SO_4^{2-}, Cl⁻ and CO_3^{2-} and (b) with SO_4^{2-}, Cl⁻ and CO_3^{2-} (each 1000 ppm).

The signals of the chromatograms for 5 ppb using AG16/AS16 column and for 4 ppb using AG20/AS20 column exhibited values 5 points greater than the noise. It is suggested that the MRL for perchlorates would be 5 ppb and 4 ppb for the AG16/AS16 and for the AG20/AS20 column, respectively. In the present study, the results were evaluated on the basis of the values obtained using the AG16/AS16 column.

3.2. Standard for ion interference

When measuring perchlorates in a complex matrix sample, the analytical sensitivity would be insignificant. Especially, general ions such as SO_4^{2-}, Cl⁻ and CO_3^{2-} exhibit a short retention time and sensitive reaction in a column for perchlorate measurement, acting as inhibitors. Fig. 2 shows the chromatograms of a sample of 25 ppb perchlorates in deionized water (a) and of a sample containing the same concentration of perchlorates in the presence of 1000 ppm of SO_4^{2-} -, Cl⁻-, and CO_3^{2-} ions (b). As the concentration of the interfering ions increased, the conductivity increased rapidly at the retention time of 3.5–4 min, decreased gradually, and affected until perchlorates were detected. Wastewater in general contains high concentration of such interfering ions which can cause an analytical error in perchlorate measurement. Therefore it is required to set a limit for the amount of interfering ions and to eliminate them with pretreatment or dilution in cases their concentration exceeds this limit.

The EPA Method 314.0 [9] recommends a preparation of a series of model solutions containing the same perchlorate concentration and adding different amounts of SO_4^{2-}, Cl⁻ and CO_3^- in deionized water. The concentration of SO_4^{2-}, Cl⁻ and CO_3^- should be maintained the same in the individual solution.

Although the ionic solutions prepared contain the same amount of SO_4^{2-}, Cl⁻ and CO_3^-, their ratio in actual samples are different. Therefore, it is more rational to use conductivity than the concentration of such ions to set the limits of the ion interference. Since the interfering ions affect the height of perchlorate peak rather than its area when analyzing samples with an IC system, the peak area to height (A/H) ratio could indicate the degree of inhibition. The conductivity, when the percent difference exceeds 20%, is set to the matrix conductivity threshold (MCT). The conductivity of samples measured should be less than the MCT.

Linear increase was observed in the relationship between the conductivity and perchlorate percent difference in the ionic solutions that have different concentrations of SO_4^{2-}, Cl⁻ and CO_3^- when measured using the AG16/AS16 column (Fig. 3) and the AG20/AS20 column (Fig. 4). The concentrations of interfering ions at 20% difference were 270 and 330 ppm, and the conductivities at the concentrations were 2236 and 2537 μS/cm,

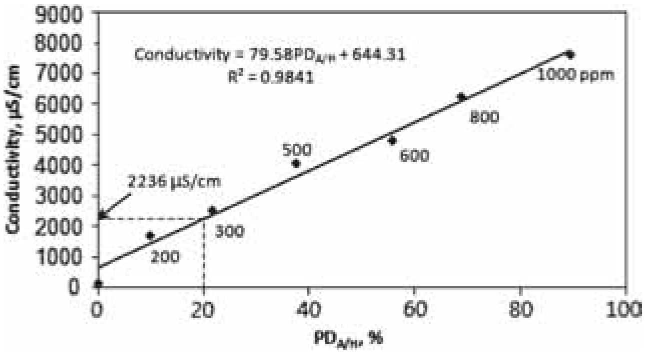

Fig. 3. The relationship between percent difference ($PD_{A/H}$) and conductivity at different concentrations of SO_4^{2-}, Cl⁻ and CO_3^{2-} for AG16/AS16 column.

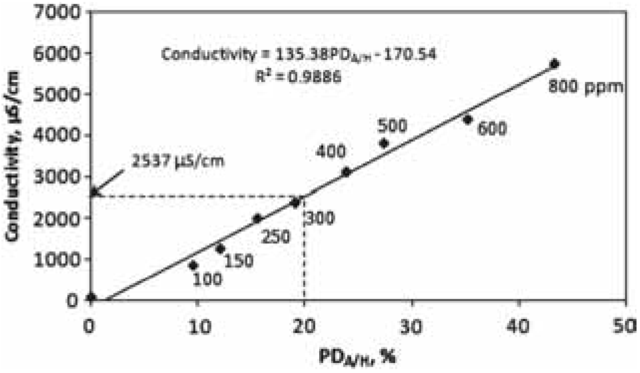

Fig. 4. The relationship between percent difference ($PD_{A/H}$) and conductivity at different concentrations of SO_4^{2-}, Cl^- and CO_3^{2-} for AG20/AS20 column.

respectively, exhibiting higher values for the AG20/AS20 column.

We also examined whether the limit for the concentration and conductivity of mixed interfering ions could also be applied to smelting wastewater because its SO_4^{2-} concentration is higher than those of the other interfering ions. Fig. 5 shows the relationship between conductivity and percent difference when the ionic solutions contain different amounts of SO_4^{2-} (only for the AG16/AS16 column). The SO_4^{2-} concentration at 20% difference was 1220 ppm, higher than those of the other ions such as Cl^- (810 ppm) and CO_3^{2-} (270 ppm). The conductivity, however, for these concentrations did not show a considerable variation (2450 µS/cm for SO_4^{2-} only and 2236 µS/cm for the mixed ions). In other words, the MCT [7] is applicable to the measurement of perchlorates in smelting wastewater when the effect of interfering ions was minimized.

It was also studied whether the SO_4^{2-} concentration and MCT could be applied for reducing the effect of inference ions when quantifying perchlorates in smelting wastewater. Fig. 6 shows the relationship between SO_4^{2-} concentration and conductivity when the wastewater discharged from a smelting factory is diluted with deionized water. The effluent exhibited the SO_4^{2-} concentration of 7450 ppm and the conductivity of 11,630 µS/cm. The effluent was diluted with deionized water and the relationship between SO_4^{2-} concentration and conductivity was similar to that of the ionic solution of SO_4^{2-} only in deionized water when the SO_4^{2-} concentration was below 2500 ppm. Thus, it is suggested that both MCT and SO_4^{2-} concentration can be used as the limit for percent difference under ca. 20% in measuring the amount of perchlorates in smelting wastewater.

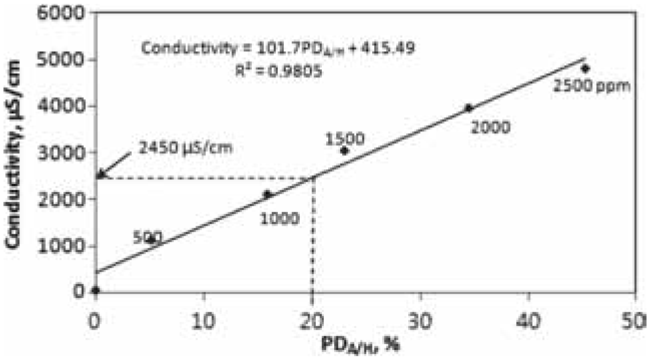

Fig. 5. The relationship between percent difference ($PD_{A/H}$) and conductivity at varying concentration of SO_4^{2-} for AG16/AS16 column.

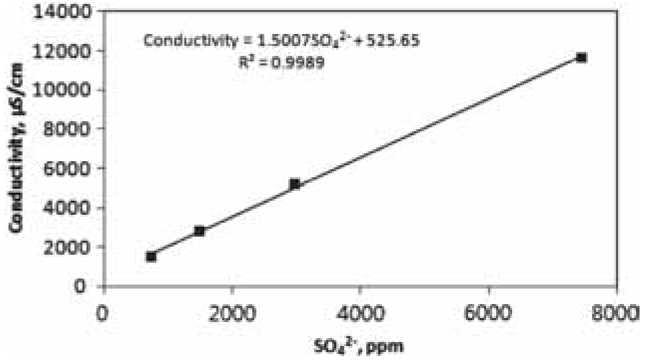

Fig. 6. The relationship between conductivity and SO_4^{2-} concentration in the diluted effluent from zinc smelting process.

3.3. Biological treatment of perchlorates in smelting wastewater

The objective of both the batch and the continuous reactor experiments was to develop a biological treatment method of perchlorates in the inorganic wastewater from the Smelting Factory A containing high concentration of dissolved inorganic compounds (Table 2). These inorganic materials inhibit microbes by increasing osmotic pressure inside the organisms, which hampers the treatment process. Kincannon and Gaudy [10] observed that microbial plasmolysis induced the increase in SCOD by 600 ppm when NaCl (4.5%) was added into the batch bioreactor containing 650 ppm of MLVSS. Pernetti and Di Palma [7] evaluated the adverse effect of Na_2SO_4 on the microbial activity. When Na_2SO_4 was applied to the aerobic bioreactor, the microbial activity decreased proportionally to the concentration of the salt. The organic matter decomposition rate decreased by 40% with the rise in the Na_2SO_4 content from 0% to 1.5% and by 80% at 3.0%-point.

Since the wastewater from the Smelting Factory A contained high concentration of dissolved inorganic compounds, it was necessary to find the range of the solids so that the biological treatment facility removes

Table 2
Physicochemical characteristics of zinc smelting wastewater

Items sample	ClO_4^- (ppm)	SO_4^{2-} (ppm)	Cl^- (ppm)	NO_3^- (ppm)	Conductivity (μS/cm)
Recycling process water	104–450	56,668–240,000	196–516	6.4	490,000–920,000
Wastewater after physicochemical treatment	8.3–25.0	6476–20,000	13.2–71.6	2.0	10,630–16,930

perchlorates at a satisfactory level. At the same time, the effect of changes in inorganic dissolved solid content on the efficiency of perchlorate removal was evaluated.

It was not possible to measure the total amount of dissolved inorganic compounds; hence SO_4^{2-} concentration and conductivity were used as alternatives. It was because the ion exhibited the highest concentration among inorganic ions contained in the wastewater from the Smelting Factory A and the conductivity was proportional to the total amount of inorganic ions. Those two indices are convenient for the continuous monitoring.

3.3.1. Effect of interfering ion on perchlorate removal

The biological treatment experiments were carried out using a series of diluted wastewater samples containing different SO_4^{2-} concentrations to evaluate the efficiency of perchlorate removal as a function of the concentration of interfering ion. The dependence of the conductivity on the SO_4^{2-} concentration is summarized in Table 3. The sample with SO_4^{2-} concentration of below 500 ppm was prepared by adding perchlorates and nutrients into tap water instead of smelting wastewater in the continuous reactor experimen

Since the diluted smelting wastewater samples contain high concentration of interfering ions, especially SO_4^{2-} causing analytical errors, it is essential to measure perchlorates under the condition of below the MCT value. To ensure this condition, perchlorates were measured after diluting the samples containing high concentration of interfering ions. The samples having the SO_4^{2-} concentrations of 8000, 12,000 and 16,000 ppm were diluted 25 times, and those of 20,000 and 25,000 ppm were diluted 50–100 times depending on the expected perchlorate concentration. Samples without smelting wastewater and with low concentration of interfering ions were not diluted. Since the maximum MDL determined in this study was 1.6 ppb, the perchlorate concentration that can be measured is 1.6 ppb for the samples without smelting wastewater. The values of the samples containing smelting wastewater were obtained by multiplying the above perchlorate concentration by the dilution of the samples. For example, the concentration of perchlorates that can be measured is 40 ppb for the samples containing SO_4^{2-} concentrations of 8000, 12,000, and 16,000 ppm.

3.3.2. Batch reactor experiment

The effect of dissolved inorganic solids on the biological degradation of perchlorates was evaluated through the batch reactor experiments. The temporal change in perchlorate concentration with varying SO_4^{2-} concentration is summarized in Figs. 7 and 8. Fig. 7 shows the experiment results conducted using microorganisms cultivated in the media whose SO_4^{2-} concentration was adjusted to the target level 1 day prior to the experiments, and Fig. 8 shows the result of the study with microorganisms cultivated for 5 days. In the absence of SO_4^{2-}, almost all perchlorates were degraded within 3 h, whereas only 55% of perchlorates were degraded within 6 h for the sample containing 8000 ppm SO_4^{2-}. For the samples with SO_4^{2-} concentrations higher than 12,000 ppm, only limited amount of perchlorates was degraded.

The batch reactor experiments were conducted again to re-evaluate the inhibitory effect of dissolved inorganic solids on the biological treatment of perchlorates after cultivating microorganisms for 5 days in each experimental condition and increasing inoculums concentration (MLVSS) to 1500 ppm. The results are summarized

Table 3
SO_4^{2-} concentration and conductivity for biological treatment of perchlorate

SO_4^{2-} (ppm)	<500	8000	12,000	16,000	20,000	25,000
Conductivity (μS/cm)	428	13,810	19,730	24,800	30,100	38,200

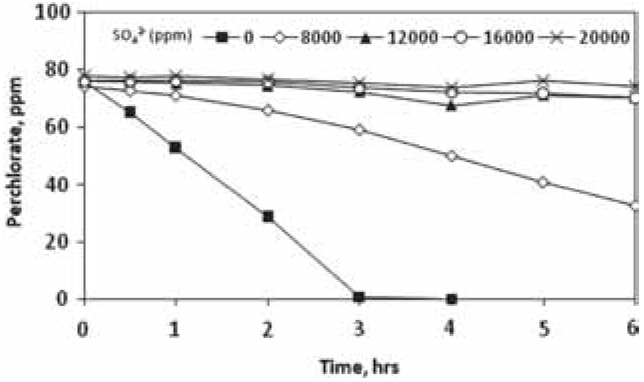

Fig. 7. Perchlorate degradation at various SO_4^{2-} concentrations (Incubation 1 day, MLVSS 650 ppm).

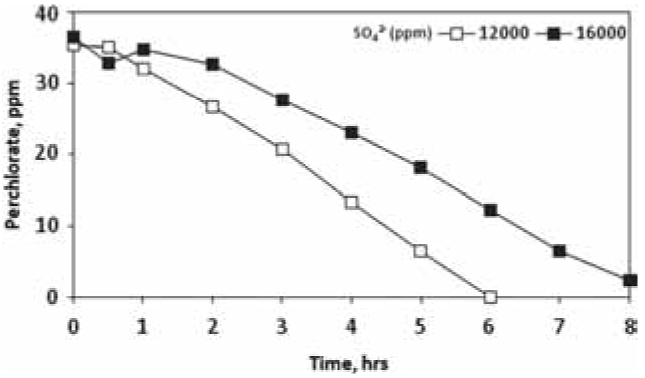

Fig. 8. Perchlorate degradation at various SO_4^{2-} concentrations (Incubation 5th day, MLVSS 1500 ppm).

in Fig. 8. The microorganisms were stabilized through 5-day acclimation and exhibited higher biodegradation efficiency than the microorganisms acclimated for 1 day. Almost all perchlorates were degraded within 6 h in the presence of 12,000 ppm SO_4^{2-} and were degraded in about 8 h under 16,000 ppm SO_4^{2-}. These results indicate that the adverse effect of dissolved inorganic solids on perchlorate degradation could be reduced by increasing the acclimation time of microorganisms and the inoculums concentration. The retention time in the biological treatment facility at the Smelting Factory A is 0.85 day. It is implied that perchlorates could be degraded to a satisfactory level in the presence of 16,000 ppm SO_4^{2-} (conductivity 24,800 μS/cm) when the microorganisms acclimated to dissolved inorganic solids were maintained above 1500 ppm MLVSS.

Since the perchlorate content decreased linearly in all the experiments after the initial acclimation time, the specific degradation rate was determined by linear regression analysis. The results are summarized in Table 4.

The perchlorate degradation rate was about 0.037/h in the absence of SO_4^{2-} and was similar to the one determined by Logan et al. [11] who studied the degradation rate using the microorganism (*Dechlorosoma* sp. KJ) isolated and cultivated in a bioreactor for perchlorate degradation. The rate decreased greatly with increasing concentration of SO_4^{2-}, and the effect of 5-day acclimation increased as well. In the presence of 12,000 and 16,000 ppm SO_4^{2-}, the degradation rates of microorganisms acclimated for 5 days increased 2.5 and 1.8 times, respectively, compared to the values obtained using the ones acclimated for 1 day.

3.3.3. Continuous treatment experiment

The efficiency of perchlorate treatment and the stability of the process were evaluated using the results of continuous treatment experiment. The retention time of anaerobic reactor was set to 0.5 day which is shorter than that of the Smelting Factory A (0.85 day), and the concentration of perchlorates in un-treated wastewater inflow was kept higher overall. The amount of inorganic ions increased gradually to the target level over 1 month, before the experiments, to induce microbial acclimation. The MLVSS in the anaerobic reactor ranged from 2000 ppm to 3000 ppm.

The perchlorate concentrations in the influent and the effluent are summarized in Fig. 9 presenting the data for experiments with influents of <500, 8000 and 16,000 ppm SO_4^{2-}. During the experiments (over 70 days), the concentration of perchlorates in the effluents was below the detection limits with exception of the first three measurement for all the influents. The maximum

Table 4
Specific perchlorate degradation rate (g-perchlorate/g-MLVSS/h) at various SO_4^{2-} concentrations

SO_4^{2-} (ppm)	0	8000	12,000	16,000	20,000
Degradation rate (h^{-1})	0.0365[a]	0.0121[a]	0.0017[a]	0.0018[a]	0.0012[a]
			0.0043[b]	0.0033[b]	

[a] Incubation 1 day, MLVSS 650 ppm.
[b] Incubation 5day, MLVSS 1,500 ppm

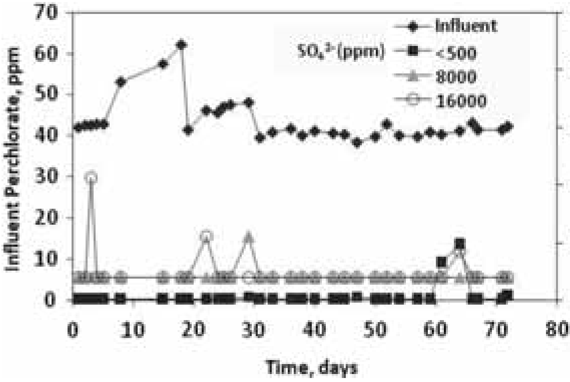

Fig. 9. The concentrations of perchlorate in influent and effluent at various SO_4^{2-} concentrations (<16,000 ppm).

perchlorate concentration in the effluents was about 0.1 ppm for <500 ppm SO_4^{2-} and slightly greater than 0.1 ppm for 8000 ppm SO_4^{2-}. For the SO_4^{2-} concentration at 16,000 ppm, the maximum perchlorate concentration reached 0.21 ppm at the initial stage of the experiment, followed by 0.1 and 0.09 ppm in two samples. The results suggest that the perchlorates can effectively and stably be removed in the presence of 16,000 ppm SO_4^{2-} (conductivity: 24,800 μS/cm).

Fig. 10 shows the concentration of perchlorates in the influents and the effluents for the experiments with the influent SO_4^{2-} concentrations of 20,000 and 25,000 ppm. The effluent perchlorate concentration rapidly increased to levels similar to the concentration in the influent on day 7 when the SO_4^{2-} concentration was elevated form 16,000 ppm to 25,000 ppm. The concentration of SO_4^{2-} at 25,000 ppm was maintained for 7 days and was lowered to 20,000 ppm after replacing the half amount of sludge by fresh one. The perchlorate concentration in the effluent gradually decreased to below the detection limits for 7 days and increased rapidly to the level similar to the concentration in the influent thereafter. These results imply that the influent containing 20,000 ppm SO_4^{2-} can be treated for short term with highly active microorganisms and that most of the microorganisms lose their activity if the condition persists. It is suggested that the maximum SO_4^{2-} concentration in influent should range between 16,000 and 20,000 ppm (conductivity: 24,800–30,100 μS/cm) for the stable biological treatment of perchlorates.

In the Smelting Factory A, the concentration of SO_4^{2-} could increase up to 20,000 ppm. Such a temporary high concentration of SO_4^{2-} in the influent would not exert an adverse effect on microbial activity, but sustained influx of influent with high SO_4^{2-} concentration requires reducing the inorganic ion contents (i.e., SO_4^{2-}) by dilution or chemical treatment.

Since in a biological treatment facility changes in characteristics and flow rates of effluent from each process of a smelting factory can change the perchlorates or dissolved inorganic solid content, we evaluated the dynamics of perchlorates, giving such a shock load. Fig. 11 shows changes in perchlorate concentration in the influent and the effluent with varying degrees of influent SO_4^{2-} concentration, which gradually increased from 3000 to 16,000 ppm. With the influent SO_4^{2-} concentration of 8000 ppm, the effluent perchlorate was not detected although the concentration of perchlorates in the influent changed rapidly from 10 ppm to 60 ppm. It should be noted that acetic acid and nutrients did not act as limiting substances and that the dosage of acetic acid should remain unchanged in order to get similar treatment efficiency in the result of this study.

As the concentration of SO_4^{2-} in the influent gradually increased (<500 $\longrightarrow$3000 $\longrightarrow$5000 $\longrightarrow$8000 $\longrightarrow$12,000 $\longrightarrow$8000 $\longrightarrow$16,000 ppm), the concentration of perchlorates in the effluent increased to 3.2–3.4 ppm almost simultaneously with the changes in SO_4^{2-} concentration. The system, however, was soon stabilized with

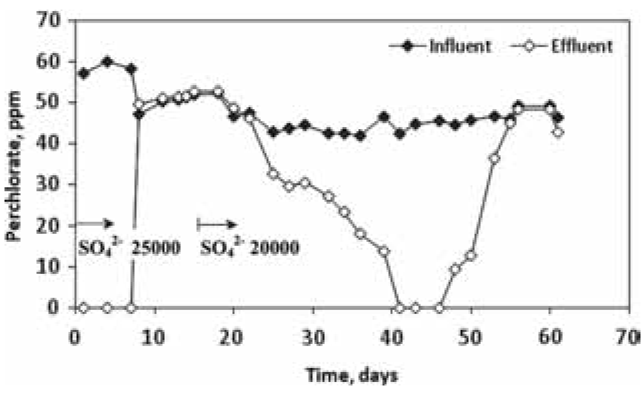

Fig. 10. The concentration of perchlorate in influent and effluent at various SO_4^{2-} concentrations (20,000 and 25,000 ppm).

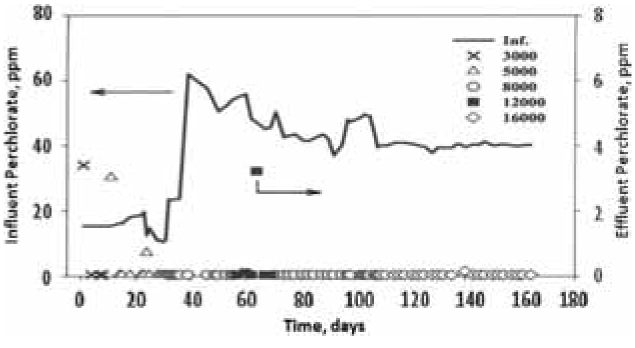

Fig. 11. The concentration of perchlorate in influent and effluent when SO_4^{2-} concentration increases gradually (3000–16,000 ppm).

the perchlorate concentration below the detection limit. After 110 days, when the system was fully stabilized, the increase in SO_4^{2-} concentration from 8000 ppm to 16,000 ppm did not induce any increase in perchlorate concentration.

Fig. 12 summarizes the variability of perchlorate concentrations in the influent and the effluent in the case of rapid change in SO_4^{2-} concentration from <500 ppm to 16,000 ppm. Three days after the change, the concentration of perchlorates in the effluent started to increase reaching a maximum of 30 ppm. After that, the perchlorate concentration gradually decreased and the system was stabilized after 40 days from the beginning. The biological treatment could degrade perchlorates under the condition of 16,000 ppm SO_4^{2-}. Once the concentration of SO_4^{2-} changes rapidly as in the experiments, which is different from gradual changes, it takes about 1 month for microbes to acclimate to the change. Therefore, it is required to establish a plan to gradually control the change in dissolved inorganic solids when such an abrupt change is expected.

3.3.4. The effect of nitrates

In smelting wastewaters containing very high concentrations of inorganic materials (i.e., SO_4^{2-} concentration of about 22,000 ppm, approximately), the perchlorates cannot be further removed due to the inhibition effect of the salts on the microorganisms. The efficiency of perchlorate treatment was evaluated with the addition of nitrate into the wastewater, which is an electron acceptor whose degradation mechanism is similar to perchlorates. A batch reactor experiment was conducted by inoculating microbes into smelting wastewater containing 35 ppm perchlorates and adding acetic acid (ca. 140 mg COD/L) as a carbon source. Another batch reactor experiment was carried out by adding 35 ppm NO_3^- into the influent wastewater prepared for the previous experiment. The changes in the acetate concentration are shown in Fig. 13. For the first experiment condition containing only perchlorates in the wastewater, the concentration of acetate rarely varied. The acetate concentration, however, decreased in the second experiment with the addition of nitrate as an electron acceptor for the growth and activity of the microorganisms. The results imply that perchlorates alone could not induce microbial growth or activity in the wastewater containing high amount of dissolved inorganic solids. However, when the electron acceptors such as NO_3^- are present, the microorganisms could grow while consuming organic material using only NO_3^- or NO_3^- with the assistance of perchlorates.

Fig. 14 depicts the changes in perchlorate concentrations in the biological treatment of smelting wastewater containing only 45 ppm perchlorates and when nitrates were added into the wastewater. Acetic acid (250 mg COD/L) was added as an exogenous carbon source in all experiments. At the initial stage of the biological treatment, most of the perchlorates were not removed.

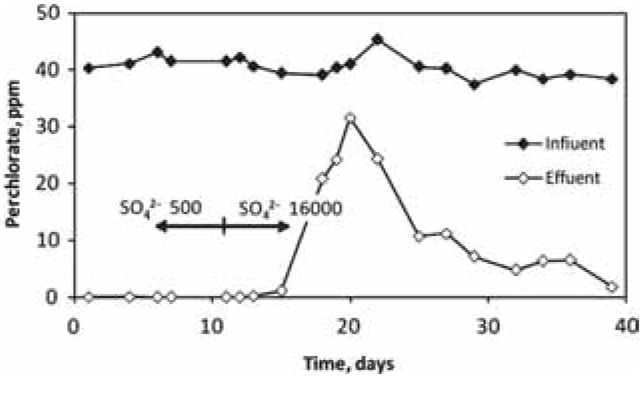

Fig. 12. The concentration of perchlorate in influent and effluent when SO_4^{2-} concentration increases rapidly (<500 →16,000 ppm).

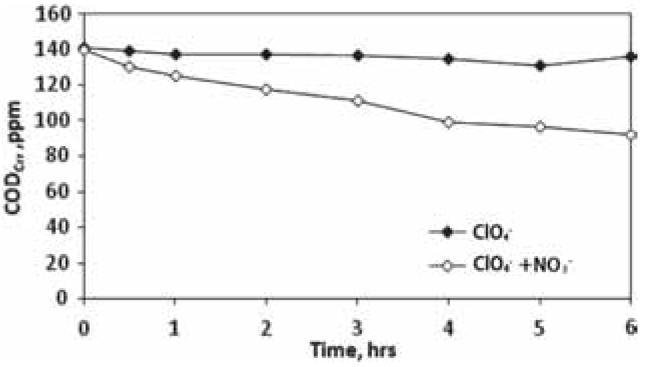

Fig. 13. COD and time variation with the addition of nitrate into batch system.

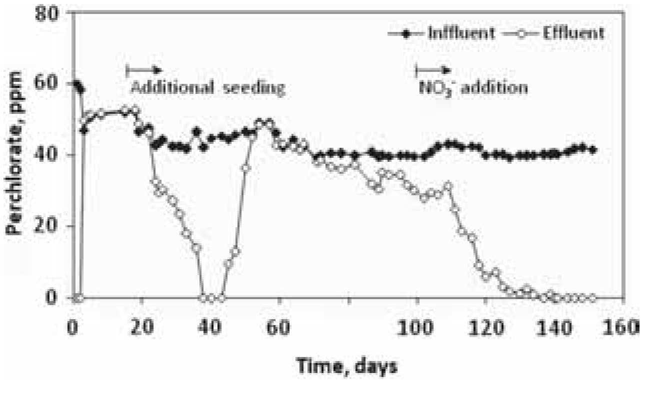

Fig. 14. Perchlorate and time variation with the addition of nitrate into continuous system

When microorganisms were additionally inoculated in the anaerobic reactor approximately 15 days after the beginning of the treatment, the perchlorate concentration in the effluent gradually decreased and almost reached zero after 40 days. However, the concentration of perchlorates in the effluent increased rapidly one week after that point, bringing their level close to that of the influent. This suggests that microorganisms exhibit little growth or activity when only perchlorates are contained in the wastewater. When NO_3^- was added (45 ppm) on the 95th day after the beginning of the treatment, the perchlorate concentration in the effluent gradually decreased and reached zero after 140 days. With the addition of NO_3^-, additional exogenous carbon source was consumed by 30 mg COD/L. However, this facilitated microbial growth and activity, and removed perchlorates almost completely.

4. Conclusions

This study demonstrated that the biological treatment can successfully remove perchlorates from the wastewater (100 m^3/d) discharged from the smelting factory A although it contains high perchlorates and dissolved inorganic solids concentrations inhibiting microbial activity.

Considering the composition of wastewater and the availability of measurement, SO_4^{2-} and conductivity were used to simulate the effect of dissolved inorganic solids. When the concentration of SO_4^{2-} increased from 0 to 16,000 ppm (conductivity: 428 $\rightarrow$ 24,800 μS/cm), the degradation rate of perchlorates decreased by 0.1 times. However, relatively high amount of perchlorates was degraded with the retention time of 0.5 day and MLVSS 2000–3000 ppm. When the influent wastewater contained 20,000 ppm of SO_4^{2-} (conductivity: 30,100 μS/cm), perchlorates could be treated only for a short term. The high concentration of SO_4^{2-} sustained in the influent for a long time inhibited microbial activity, so it was required to reduce the amount of SO_4^{2-} and other inorganic dissolved ions in the influent by the enhanced dilution or chemical treatment.

When the wastewater contained perchlorates and high concentrations of dissolved inorganic solids (SO_4^{2-} 22,000 ppm) included perchlorates only, microbial activity and growth were limited. However, the presence of electron acceptors such as NO_3^- in the wastewater, along with perchlorates, accelerated microbial activity and growth, which helped to degrade perchlorates.

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