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Electrocoagulation with a nanosecond pulse power supply to remove COD from municipal wastewater using iron electrodes

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Electrocoagulation (EC) with iron electrodes was used to remove the chemical oxygen demand (COD) of municipal wastewater. A nanosecond pulse power supply (NSP) was evaluated and compared with direct current (DC). During the EC process, municipal wastewater was collected from the sewage center in Nagaoka City, Japan. Four Fe electrodes were connected in a monopolar parallel configuration (MP-P). The obtained results indicated that the maximum COD removal efficiencies were 72 % and 82 % using DC and NSP, respectively. The use of an NSP allows EC operation at high voltage without the breakdown of the medium between the electrodes, promoting iron hydroxide flocs and the quantity of hydrogen bubbles as well as enhancing the COD removal efficiency with low specific energy consumption (SEC). At a similar COD removal efficiency (~ 72 %), compared with DC, an NSP could reduce the SEC by approximately 40 %. Therefore, compared with DC, the use of an NSP allows low-cost operation and enhances the COD removal efficiency from municipal wastewater. Analysis of the electrochemically generated byproducts by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and energy dispersive spectroscopy (EDS) showed that NSP flocs had higher adsorption properties for pollutants than DC flocs. The results permitted us to conclude that an NSP could be useful for promoting the spread of EC and the use of renewable energy sources for wastewater treatment to reduce the carbon footprint of the entire process.

Keywords: Electrocoagulation, iron electrode, COD, nanosecond pulse, specific energy consumption.

1. INTRODUCTION

Chemical oxygen demand (COD) is a measure of the amount of oxygen used in the chemical oxidation of organic matter and oxidizable inorganic matter present in water or wastewater. The COD in water increases due to the presence of biodegradable organic, nonbiodegradable and inorganic oxidizable compounds [1, 2]. The COD is not a specific parameter, but it is widely used as a traditional parameter and is useful for evaluating water quality.

Municipal wastewater is one of the main problems currently encountered in developing countries and comes from different discharge sources, such as residences, institutions, commercial and industrial buildings and groundwater; surface water could also be present [3]. This wastewater is harmful to the natural environment if it is not treated before discharge and can contaminate land and water bodies. Eutrophication is one of the main consequences [4]. Accordingly, a wastewater treatment plant (WTP) is necessary to remove pollutants from municipal wastewater, thus avoiding negative effects on the environment and human health. However, a WTP is not a preference in developing countries because the benefits are not directly received. Furthermore, operating and maintaining a WTP is quite expensive [5]. Therefore, finding a suitable technology with low operation and maintenance costs is necessary for developing countries. In this work, electrocoagulation (EC) is introduced as a promising wastewater treatment process, and compared with the use of a direct current (DC), a nanosecond pulse was applied as the main power supply to enhance the COD removal efficiency and reduce the specific energy consumption (SEC).

EC has been applied for a long time. However, the high cost of electricity is the main reason for its limited use in industrial applications [6, 7]. Currently, there are many renewable energy sources that can lead to reduced energy costs, promoting new interest in the EC process for treating wastewater. Moreover, the use of renewable energy sources with EC is highly desirable to promote an ecofriendly route for wastewater treatment [8]. Recently, EC has been applied to remove COD from many wastewaters, including those from the tannery and textile industries [9], refineries [10], the food industry [11], the paper industry [12], produced water [13], etc.

EC is an advantageous technology compared with other conventional methods due to its unique features, such as complete degradation of pollutants, minimal sludge generation, simple design, reduced or no chemical addition, and rapid sedimentation of the electrogenerated flocs [14]. During EC, metal hydroxide flocs are generated *in situ* as an electric current passes through electric electrodes. These flocs act as coagulants to adsorb pollutants in solution. Because the flocs are relatively large, contain less bound water and are stable, they can be easily removed by filtration [15].

Normally, DC and alternating current (AC) are used as the main power supply for EC operation [16]. In the present study, a nanosecond pulse power supply (NSP) was proposed to enhance the COD removal efficiency from municipal wastewater with low SEC. In the existing literature, little or no consideration has been paid to a comparison between an NSP and DC based on the COD removal efficiency and SEC. Therefore, this work aimed to focus on this comparison. Furthermore, this study also focused on comparing the characteristics of the EC byproducts generated from the DC and NSP by using X-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and field emission scanning electron microscopy (FE-SEM), which no studies have investigated to date.

Generally, Al and Fe materials are used as electrodes for EC due to their abundances on Earth and low price. Moreover, iron and aluminum hydroxides form with low toxicity and high valence, which leads to a high removal efficiency for pollutants [16]. In this work, Fe was used as the main electrode material. The main reaction that occurs at the anode during EC [17, 18] is as follows:

$$\mathrm{Fe} - 2e^{-} = Fe^{2+} \qquad (1)$$

Simultaneously, a cathode water reduction reaction occurs to generate hydroxyl ions (OH^{-}) and hydrogen gas.

$$H_2O + e^{-} = \frac{1}{2}H_2 + OH^{-} \qquad (2)$$

The final products are strongly dependent on the reaction rate of Fe^{2+} oxidation to Fe^{3+}, pH and oxygen saturation conditions in nonelectrochemical processes. Under alkaline conditions, Fe^{2+} will immediately oxidize to Fe^{3+} (pH = 7.6-14) [19]. In this study, the initial pH of 7 of wastewater was used. However, the final pH values were 10.5 and 8.1 after 90 min (data not shown) of EC with DC and an NSP, respectively. Therefore, the Fe^{2+} ion could be oxidized easily to Fe^{3+} because oxygen is present in solution as follows [17]:

$$Fe^{2+} + OH^{-} = Fe(OH)_2 \qquad (3)$$

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O = Fe(OH)_3 (4)$$

2. MATERIALS AND METHODS

2.1. Test wastewater

Municipal wastewater samples were taken from the sewage treatment center of Nagaoka City, Japan. Table 1 shows some representative parameters of the municipal wastewater.

Table 1. Characterization of the municipal wastewater

Parameter	Unit	Value
pH	-	7.1
Chemical oxygen demand (COD)	mg/L	177
Dissolved oxygen (DO)	mg/L	0.16
Electrical conductivity	mS/m	61.2
Total nitrogen (TN)	mg/L	28.6
Total phosphorous (TP)	mg/L	3.5

The pH and electrical conductivity were measured before and after the experiment using a pH meter (Model HM-30R, range from 0.000-14) and COND meter (Model ES-71), respectively. The COD and TN were measured using the Hach Method 8000. The TP was determined by the Hach Method 8190. The DO was measured by following Hach Method 8166. Each experiment was performed at least three times to confirm the results. In addition, chemical and physical characterizations were performed by using EDS, FE-SEM (JEOL JSM-6700F) and XRD (Rigaku RINT-2500, CuKα).

The COD removal efficiency (η) at time *t* is defined as follows:

$$\eta(t) = \frac{COD_0 - COD_t}{COD_0} \qquad (5)$$

where COD_0 and COD_t correspond to the initial COD and the COD at time *t*, respectively.

SEC is a fundamental assessment for any treatment method to evaluate its feasibility on a large scale.

The SEC using an NSP source can be calculated as follows:

$$SEC_{NSP} = \frac{\int_{t_1}^{t_2} u(t)i(t)dt \times f \times \tau}{3.6 \times 10^6 \times v} \qquad (6)$$

where SEC_{NSP} corresponds to the NSP SEC (kWh/m^3), u(t) is the voltage function (V), i(t) is the current function (A), t_1 and t_2 are the time range for a single pulse (s), *f* is the pulse repetition frequency (Hz), τ is the treatment time (s), and v is the wastewater volume (m^3).

Equation (6) can be simplified when a DC source is used as follows:

$$SEC_{DC} = \frac{UIT}{1000\,v} \qquad (7)$$

where SEC_{Dc} corresponds to the DC SEC (kWh/m^3), *U* is the applied voltage (V), *I* is the current intensity (A), and T is the treatment time (h).

2.2. Experimental setup

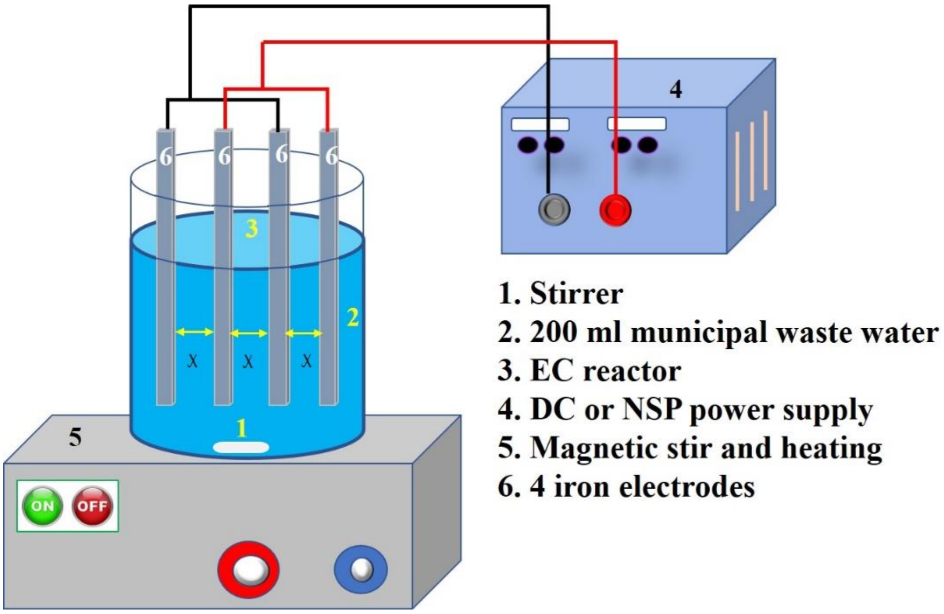

Figure 1. Schematic of the laboratory-scale EC reactor setup (the same separation in all cases, χ=1 cm).

Fig. 1 shows the experimental setup for the EC of 200 ml of wastewater. Four iron electrodes were connected in a monopolar parallel connection (MP-P). All electrodes, 1x20x55 mm^3 in size, were equally arranged (*x*=1 cm), as shown in Fig. 1.

Both power supplies, PL-650-0.1 (DC) and HK-10N (NSP) from Matsusada Precision Inc. (Japan) were used in the potentiostatic mode. The appropriate voltage ranges to avoid breakdown of the medium between the electrodes were determined to be V_{DC} = {1 to 5 V} for DC and V_{NSP} = {1 to 50 V} for the NSP.

During the EC process, a magnetic stirrer was used at 200 rpm and room temperature to enhance the contact between the pollutants and the formed metal hydroxide adsorbent.

3. RESULTS AND DISCUSSION

3.1. Effect of the applied voltage on the COD removal efficiency

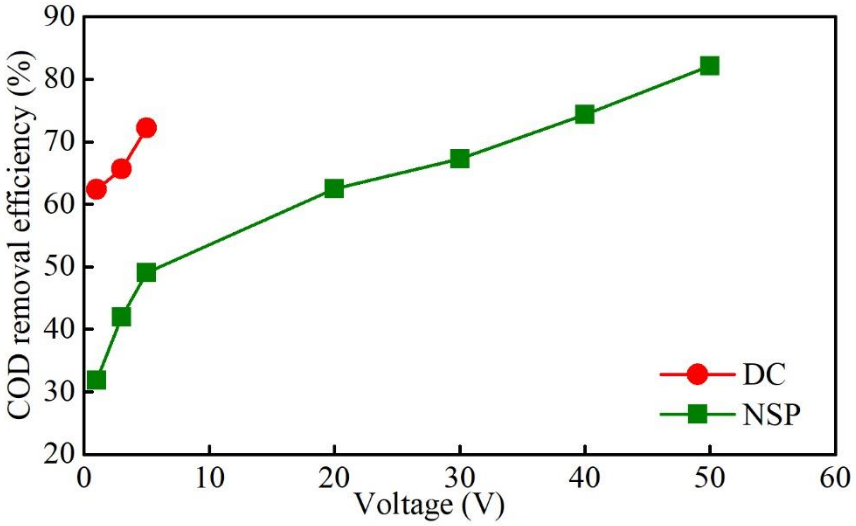

Figure 2. Effect of the voltage on the COD removal efficiency with a treatment time of t=90 min using DC and an NSP (pulse width (pw) 1 μs, frequency (f) 10 kHz).

The effect of different applied voltages on the COD removal efficiency was investigated by running the EC process using different DC and NSP voltages of 1, 3, and 5 V for DC and 1, 3, 5, 20, 30, 40, and 50 V for the NSP. The results are displayed in Fig. 2. As expected, regardless of whether DC or an NSP was used, the COD removal efficiency increased with the applied voltage. This increase can be explained by the fact that the applied voltage can not only determine the dosage rate of the coagulant but also promote the quantity of hydrogen bubbles, thus enhancing the flotation efficiency [20]. Therefore, the applied voltage influences the COD removal efficiency from municipal wastewater. According to Faraday's law, as the applied voltage increases, the efficiency of ferrous or ferric ions released into the medium from the respective electrodes also increases at a certain time. As a result, the quantity of ferrous or ferric hydroxide flocs available to remove colloidal particles increases, thus enhancing the COD removal efficiency. At that time, the hydrogen bubble evolution at the cathodes also increases with the applied voltage, promoting the COD removal efficiency by flotation [20, 21].

As shown in Fig. 2, regardless of the use of DC or an NSP, the COD removal efficiency rapidly increased in the low voltage range of 1-5 V. However, it is interesting to note that the influence of DC on the COD removal efficiency is more significant than that of the NSP in this range. The results show variation in the COD removal efficiency from 62-72 % and 32-49 % in the case of DC and the NSP, respectively.

DC and the NSP were found to operate best in different applied voltage ranges (see Fig. 2). The maximum applied voltage in the case of DC was 5 V to avoid breakdown of the EC cell medium, whereas the NSP can be used up to 50 V with no breakdown observed. These results lead to differences in the maximum COD removal efficiency when using DC or the NSP, i.e., 72 % and 82 %, respectively.

On the other hand, Fig. 2 shows that a 5 V DC and 40 V NSP led to a similar COD removal efficiency ($\eta \sim 72$ %). Therefore, the DC 5 V and NSP 40 V configurations were used to simplify the comparison and discussion between DC and the NSP.

3.2. Relationship between the SEC and applied voltage

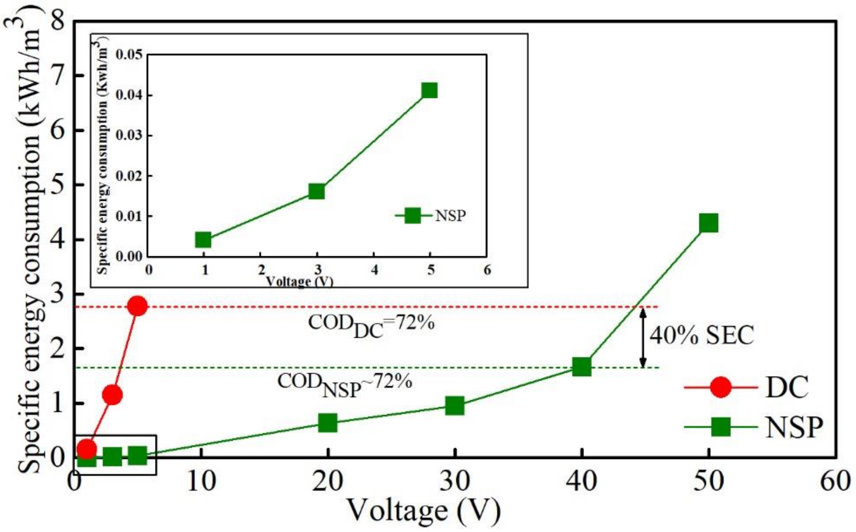

Figure 3. The SEC as a function of the applied voltage with a treatment time of 90 min (pw =1 μs, f =10 kHz).

Fig. 3 shows the variation in the SEC upon increases in the applied voltage. Whether DC or an NSP was used, an increase in the applied voltage from 1 to 5 V (DC) or 1 to 50 V (NSP) led to an increase in the SEC from 0.2-2.8 kWh/m^3 or 0.004-4.3 kWh/m^3, respectively. As shown in this figure, the SEC in the case of DC increased rapidly compared with the SEC of the NSP. The results can be attributed to the fact that when DC is used, the input voltage is constantly transferred to the electrodes. In contrast, EC is only active when a pulse is available (time -ON) in the case of the NSP. Notably, the SEC of the NSP was always below the SEC of DC over the entire applied voltage range.

Fig. 3 and the Fig. 3 inset show that in the lower range of applied voltages of 1-5 V, the NSP exhibited a low SEC, increasing from 0.004-0.041 kWh/m^3, whereas the SEC is several orders of magnitude higher from 0.2-2.8 kWh/m^3 in the case of DC. The results are in excellent agreement with the results shown in Fig. 2. This agreement may be attributed to the direct proportionality between the SEC and potential electrolysis and implies that a high SEC leads to the generation of more ferrous or ferric ions, enhancing the formation of the ferrous or ferric hydroxides needed to coagulate soluble organic compounds and metal ions and resulting in the increasing COD removal efficiency [22, 23]. Therefore, in the case of the NSP, the COD removal efficiency was only 32-49 % compared with 62-72 % using DC in this range of applied voltages (Fig. 2).

The SEC values of DC 5 V and NSP 40 V were 2.8 and 1.7 kWh/m^3, respectively. At a similar COD removal efficiency (η ~ 72 %), the use of an NSP consumed approximately 40 % less SEC than DC (Fig. 3).

3.3. Effect of the treatment time on the COD removal efficiency and SEC

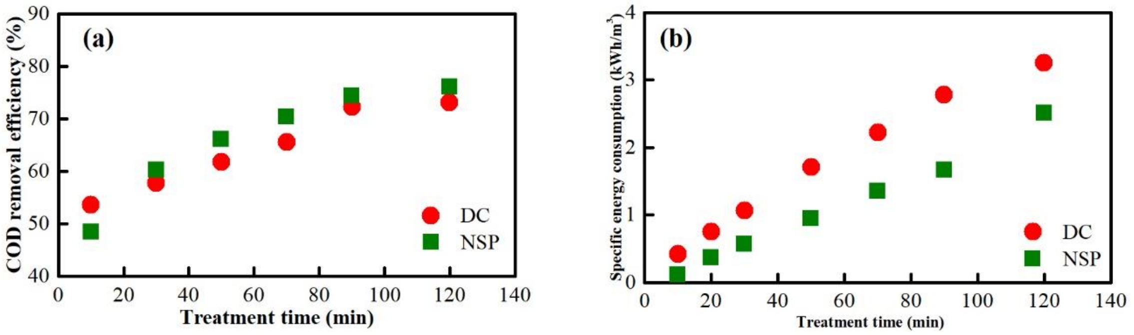

Figure 4. Effect of the treatment time on the COD removal efficiency (a) and SEC (b) for DC 5 V and NSP 40 V (pw = 1 µs, f = 10 kHz).

Fig. 4 shows the effect of the treatment time on the COD removal efficiency and SEC. In this present investigation, the EC treatment time was studied in the time range of 10, 30, 50, 70, 90, and 120 min. Regardless of whether DC or the NSP was used, the COD removal efficiency increased proportionally within the first 90 min of EC, from 53 to 70 % and 48 to 76 %, respectively (Fig. 4a). This increase could be attributed to the quantity of ferrous or ferric ions generated from the anode increasing, thus enhancing ferrous or ferric hydroxide formation, which in turn trap pollutants and promote the COD removal efficiency [24]. In addition, more hydrogen bubbles were generated at the cathode over time. This trend was beneficial in terms of a high pollutant removal efficiency through flotation by hydrogen gas and consequently increased the percentage of pollutant removal [25, 26].

However, after 90 min of EC, there was no significant effect of the treatment time on the COD removal efficiency (< 2 %). This trend could be explained by at least two reasons: a) a sufficient number of flocs were available to remove the pollutants [15] and b) the decreasing cathode reduction and formation of new electrocoagulant flocs [27].

Figure 4b shows that regardless of whether DC or an NSP was used, the SEC increased constantly with time. Notably, the use of an NSP produces a systematically higher COD removal efficiency and requires less energy than DC for the entire treatment time.

3.4. Relationship between the COD removal efficiency and SEC

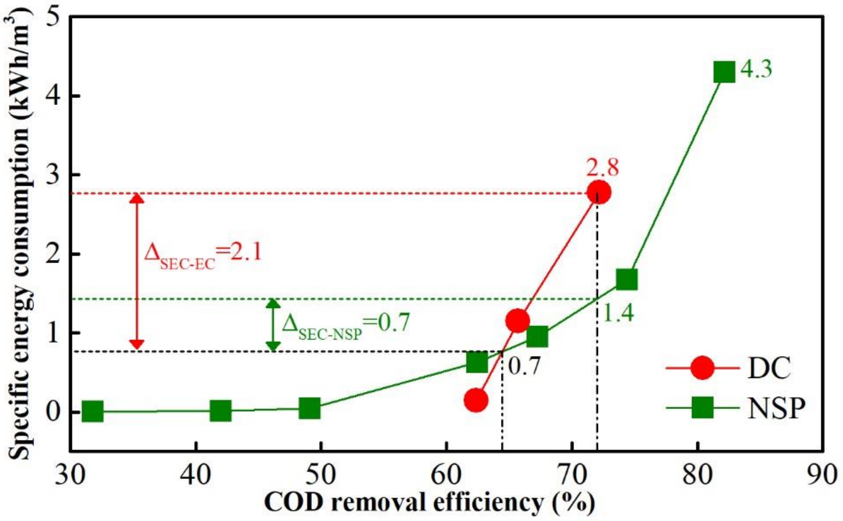

Figure 5. The relationship between the SEC and COD removal efficiency using DC and an NSP (pw = 1 µs, f = 10 kHz) with a treatment time of 90 min and an applied voltage range from 1-50 V.

Fig. 5 presents the rate of change in the SEC as a function of the COD removal efficiency. In the case of DC, the SEC rapidly increased compared with the SEC of the NSP with the COD removal efficiency. With both DC and the NSP, the SEC required approximately 0.7 kWh/m^3 to reach a COD removal efficiency of 64 %. In the case of DC, EC required 2.8 kWh/m^3 ($\Delta_{SEC\text{-}DC}$ = 2.1 kWh/m^3) to enhance the COD removal efficiency to a maximum of 72 %. However, the NSP only required 1.4 kWh/m^3 ($\Delta_{SEC\text{-}NSP}$ = 0.7 kWh/m^3) SEC to increase the COD removal efficiency to 72 % (see dashed line). Therefore, using a DC power supply can consume at least three times more energy than an NSP. Therefore, the results indicate that the SEC was more efficient for the NSP than DC to remove COD from municipal wastewater. Furthermore, using an NSP allows for a higher COD removal efficiency (η=82 %) to be obtained at a high SEC of 4.3 kWh/m^3.

In addition, Fig. 5 shows that DC was recommended for use at low SEC due to no significant enhancement in the COD removal efficiency ($\Delta\eta$~5 %) as the SEC increased.

3.5. Characterization of the byproducts from the EC cell

The morphology of the precipitates from the EC reactor are shown in Fig. 6. The FE-SEM observation shows that the precipitate has a porous surface in the case of DC (Fig. 6a). Meanwhile, in the case of the NSP, the surface of the precipitate includes smaller particles stacked over each other (Fig. 6b); hence, the higher surface area of the NSP colloids favors denser floc formation compared to the DC flocs [28].

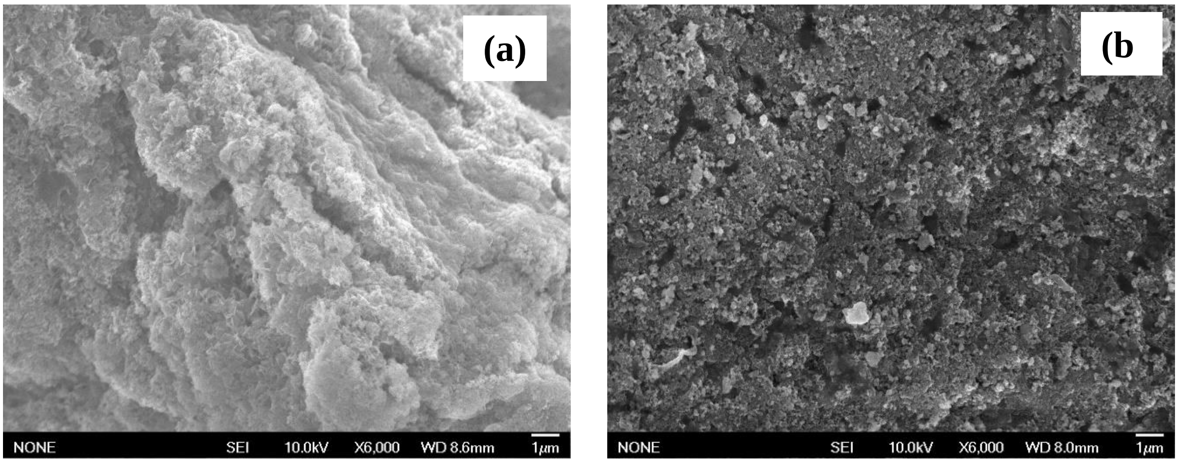

Figure 6. FE-SEM images of EC byproducts: (a) DC and (b) NSP.

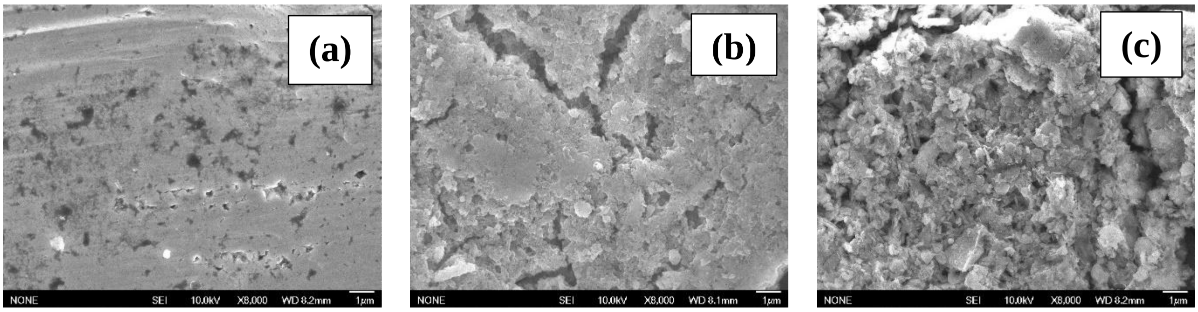

Figure 7. FE-SEM images of the anode electrode surface before EC (a) and after using an NSP (b) and DC (c).

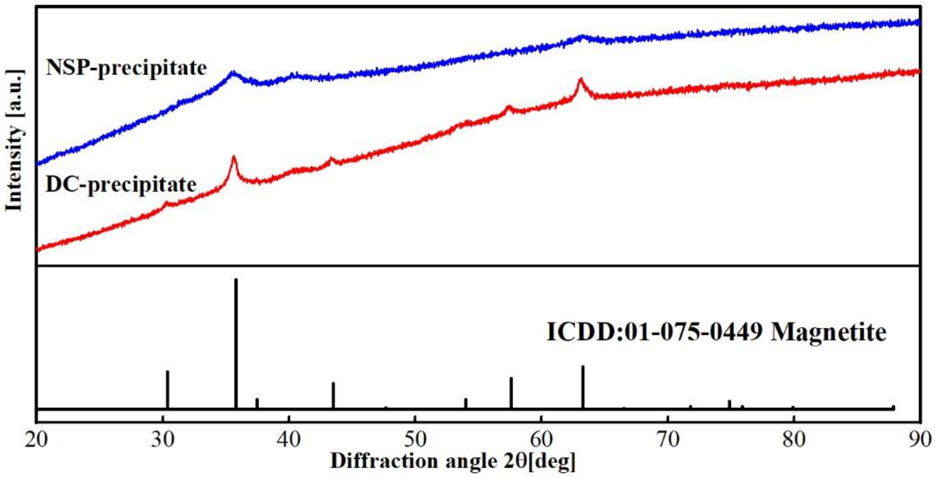

Figure 8. XRD patterns of the EC byproducts with DC and NSP power supplies.

To further understand the effects of the DC and NSP on the electrodes, the morphology of the electrode surface with both power supplies was observed by FE-SEM (Fig. 7(a), 7(b) and 7(c)). The results reveal that the surface of the electrode had few disordered pores and a smooth microstructure, which suggests that the iron electrodes dissolve uniformly during EC using the NSP (Fig. 7b). However, in the case of DC, the surface of the iron electrodes was rough, and there were many indentations (Fig. 7c). The indentations can be attributed to consumption of the anode material at active sites because of the generation of oxygen evolution at the surface [29].

Fig. 8 shows the XRD diffraction patterns of the precipitates obtained using DC and the NSP. The XRD signal intensity of the precipitate in the case of the NSP was slightly lower than that of the precipitate from DC. This difference is probably because the precipitate from the NSP was better at adsorbing organic pollutants during settling than that from DC [28]. Moreover, the XRD peaks of the DC and NSP precipitates were found to match the ICDD values of magnetite (ICDD: 01-075-0449). The magnetite phase has also been reported elsewhere on Fe electrodes used for EC [30-32].

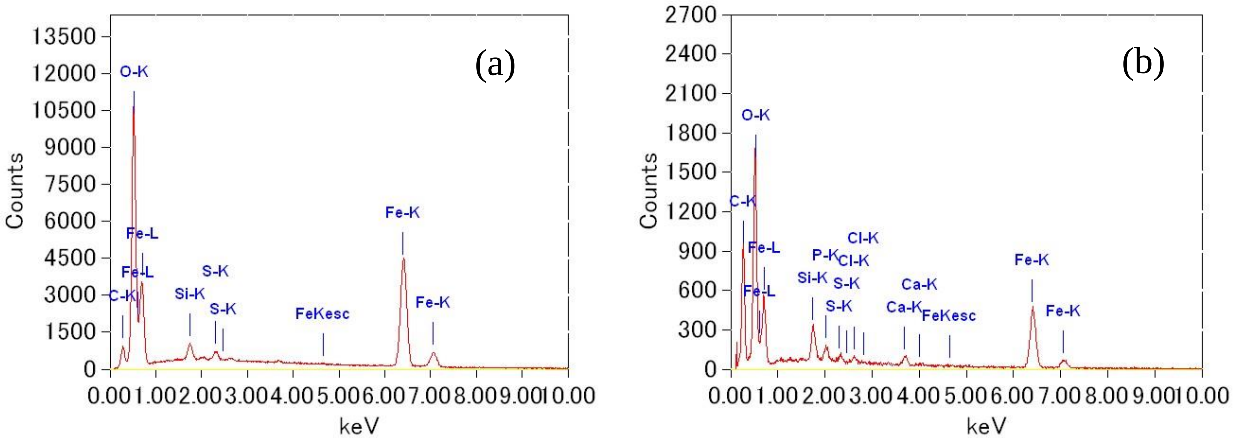

Figure 9. EDS analysis of the EC byproducts with DC (a) and an NSP (b).

Fig. 9 depicts the EDS analysis of the DC and NSP precipitates. Regardless of whether DC or the NSP was used, S, Si, C, and O were adsorbed on the precipitate. Moreover, apart from the above elements, Cl, P and Ca appeared in the NSP precipitate (Fig. 9b). Therefore, it is worth noting from Fig. 8 and Fig. 9 that using an NSP could result in better EC performance than DC because the adsorption ability of the precipitate from the NSP was better than that from DC.

4. CONCLUSIONS

The present study demonstrates EC using Fe electrodes with the application of an NSP and DC power supply to remove COD from municipal wastewater. The results show that the highest COD removal efficiency was 72 % at 5 V and 82 % at 50 V using DC and an NSP, respectively. Moreover, at a similar COD removal efficiency, compared with DC, the NSP could reduce the SEC by 40 %. The FE-SEM, XRD and EDS studies confirmed that the NSP-generated flocs were better for adsorbing pollutants than DC-generated flocs. The results permit us to conclude that the use of an NSP not only increases the COD removal efficiency but also reduces the operational cost of wastewater treatment facilities. Therefore, it promotes the use of the EC process that should ideally be coupled with renewable energy to reduce the carbon footprint of wastewater treatment.

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