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A comparative study of waste activated sludge disintegration by electrochemical pretreatment process combined with hydroxyl and sulfate radical based oxidants

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ABSTRACT

In this study, electrochemical treatment (EC) combined with hydrogen peroxide (HP), calcium hypochlorite (CHC), peroxymonosulfate (PMS) and peroxydisulfate (PDS) was investigated as a pretreatment process for improving waste activated sludge (WAS) disintegration in terms of soluble chemical oxygen demand (sCOD). A pair of Fe-Fe electrodes were used in the study, and the main operation parameters were determined as oxidant dosage, initial pH, applied current, electrolysis time and concentration of electrolyte solution (Na_2SO_4). The maximum disintegration degrees in terms of the COD (DD_{COD}) values were found 11.80 %, 11.11 %, 9.61 % and 10.65 % for EC combined with HP, CHC, PMS and PDS treatments at the optimized conditions, respectively. DD values were also calculated for total organic carbon (TOC) and total nitrogen (TN) concentrations after the pretreatment at the optimum conditions, and lower DD_{TOC} values and almost equal DD_{TN} values to DD_{COD} were obtained. Capillary suction time analyses were performed to determine WAS dewaterability, and reductions of 27.34 %, 29.25 % and 36.13 % CST were found for EC combined with the CHC, PMS and PDS treatments, respectively. EC-HP combination did not enhance WAS filterability, as the CST value increased from 13.1 s of raw sludge to 18.1 s of HP-treated sludge. Extracellular polymeric substance (EPS) types and concentrations were also investigated at the optimized conditions, and the concentrations of polysaccharide and protein increased in soluble EPS (S-EPS). On the other hand, both protein and polysaccharide components decreased in loosely-bound EPS (LB-EPS) and tightly-bound EPS (TB-EPS) in almost all treatments. EC-HP pretreatment was found to be the best combination in order to enhance disintegration of WAS, whereas EC-PDS combination was the best for WAS dewaterability, among all treatment application.

1. Introduction

High amounts of waste activated sludge (WAS) are generated in biological wastewater treatment plants (WWTP) where municipal and light industrial wastewater are treated concurrently in order to protect the environment and human health [1,2]. Approximately 50–60 % of total operating costs of WWTPs consist of WAS treatment and management [3,4]. Today, proper disposal of WAS is a foremost problem as inappropriate disposal of WAS will cause environmental pollution. WAS mainly contains organic matter, bacterial microorganisms and some nutrients such as nitrogen and phosphorus [5,6]. Due to the higher organic matter contents and pathogen contaminations, anaerobic digestion, which is one of the most common and efficient methods, is used for the stabilization of WAS in large-scale WWTPs [7].

As well known, 3 stages, hydrolysis, acetogenesis and methanogenesis, take place during anaerobic digestion of waste sludge, and the first stage of this process is generally the rate-limiting step [8,9]. Polysaccharides, proteins, lipids and soluble inert materials trapped in the microbial cell walls and sludge floc structure, lead to difficulties in organic matter release [7,10]. To overcome this, pretreatment processes such as, mechanical [11,12], chemical [13–16], thermal [17,18], biological [19–21] advanced oxidation processes (AOPs) [22,23] have been tested to accelerate the hydrolysis step and enhance sludge solubilization and disintegration [1]. After pretreatment, microorganism cell walls were substantially disrupted, sludge flocs were disintegrated, and intracellular substances of microbial cells were released into the filtrate. These released components can be readily biodegradable. Thus, the hydrolysis stage of anaerobic digestion is accelerated, and methane production is promoted [1,24]. However, the some of aforementioned pre-treatment processes have some

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drawbacks, such as high chemical consumption for chemical pretreatment, high energy demand for physical pretreatments and slow process of biological pretreatment [1,25]. On the other hand, AOPs are significantly effective and economical pretreatment methods for WAS disintegration and dewaterability. Highly reactive hydroxyl and/or sulfate radicals (˙OH and $^{\cdot}SO_4^{2-}$) produced in-situ react with organic substances unselectively, accelerating solubilization and mineralization of microbial flocs [26,27].

The Fenton process is one of the widely used methods of AOPs due to homogenous ˙OH generation. The main drawback of the Fenton process is requirement of a large amount of hydrogen peroxide (HP), which is a limitation, in WAS treatment [26,28]. Electrochemical treatment combined with HP (also called electro-Fenton process) could overcome this drawback of the conventional Fenton process [29]. Eq. (1) and Eq. (2) occur in Fenton process.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2{}^{\cdot} \quad (2)$$

According to Eqs. (1) and (2), ferrous ions and HP use under acidic conditions in Fenton process and produces ˙OH subsequently. Hydroperoxyl radicals ($HO_2{}^{\cdot}$) and organic radicals are also produced during this process and these oxidant species may react more slowly than the ˙OH [30].

The EC combined with HP treatment was more pH sensitive than the EC process. It was reported that WAS disintegration decreased at higher pH values above 3, due to the production of ferric hydroxide and other ferric species. The generation of these species causes quick decomposition of HP to water and O_2, leading to lower oxidative capacity. Furthermore, the Fe^{3+} precipitation in the form of $Fe(OH)_3$ inhibits the reaction between Fe^{3+} and HP and then affects the regeneration of Fe^{2+}. Under higher pH values (>8.0), $Fe(OH)_4{}^-$ dominates compared to other Fe^{3+} compounds, resulting in the production of flakes that finaly decline the disintegration of WAS [31]. On the other hand, releasing a higher amount of Fe^{2+} and Fe^{3+} through anodic metal dissolution led to coagulation, thereby more bubbles were generated at the cathode resulting in flotation [30].

On the other hand, hypochlorite is another commonly used oxidant due to easy reaction of chlorine with the organic materials of the microbial cell. Thus, chemical oxidation or electrochemical oxidation with hypochlorite (ClO^-) may provide effective pretreatment of WAS. Fe^{2+} as the catalyst plays an important role in producing ˙OH in $Fe^{2+}/Ca(ClO)_2$ oxidation process. The ˙OH is expected to generate via the reaction between Fe^{2+} and HOCl (Eq. (3)) [32]. Zhu et al. [32] also reported that the further increase of $Fe^{2+}/Ca(ClO)_2$ (above 1.25) did not enhance the WAS dewaterability which could be attributed to the reduced ˙OH due to direct reaction of ˙OH with excess Fe^{2+} (Eq. (4)).Ye et al. [1] reported that EC-combined ClO − pretreatment at the ClO − dosage of 0.6 % was found economically feasible based on their economic evaluation.

$$Fe^{2+} + HOCl \rightarrow Fe^{3+} + {}^{\cdot}OH + Cl^- \quad (3)$$

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH– \quad (4)$$

Apart from these hydroxyl-based oxidants, sulfate-based oxidants such as peroxymonosulfate (PMS) and peroxydisulfate (PDS) are also widely used in WAS treatment in recent years [33,34]. An innovative combination of electrolysis and iron-activated persulfate oxidation was investigated by Zhen et al. [35] and Li et al. [36] for enhancing the dewaterability of waste activated sludge, and it was reported that electrolysis combined with PDS/Fe^{2+} pretreatment could effectively enhance the dewaterability of WAS due to disruption of the protective barrier of microbial cells that lead to water release. Eqs. (5) and (6) show the occurred reaction in Fe^{2+} activated PMS and PDS oxidation [34,37].

$$Fe^{2+} + HSO_5{}^- + Fe^{3+} + {}^{\cdot}SO_4{}^{2-} + OH^- \quad (5)$$

$$S_2O_8{}^{2-} + Fe^{2+} \rightarrow {}^{\cdot}SO_4{}^{2-} + Fe^{3+} + SO_4{}^{2-} \quad (6)$$

Recently, electrochemical (EC) pretreatment of WAS by using different metal electrodes and different oxidants has been investigated to improve sludge disintegration and dewaterability [1,4,30,38–40]. Generally, a pair of Ti/Ti, Ti/RuO_2 or Ti/IrO_2 mesh plate electrodes were used in these studies, and disintegration degrees in terms of COD were enhanced in a wide range between 1.6 % and 30.2 % [7,38–41]. Moreover, several studies were conducted on the EC process combined with oxidants such as hypochlorite, hydrogen peroxide and persulfate for pretreatment of WAS [6,29,36,42]. The authors reported in these studies that EC combined processes with these oxidants enhanced the disintegration degree (DD) and dewaterability of WAS.

Although different hydroxyl or sulfate radical-based oxidants have been investigated in EC pretreatment of WAS, a comparative study that investigated WAS pretreatment by the EC process combined with both hydroxyl and sulfate radical-based oxidants has not been encountered. Therefore, the main aim of this study is to investigate the impact of different oxidants on WAS disintegration in the EC pretreatment process. In the study, main operating parameters, namely the oxidant dosage, initial pH, applied current, electrolysis time and electrolyte solution concentration were optimized, and the DD values of WAS were determined via soluble chemical oxygen demand (sCOD) content during laboratory optimization experiments for each oxidant. In the determined optimum conditions, DD values were also determined by means of TOC and TN concentrations. Furthermore, the CST values of WAS and the protein and polysaccharide concentrations of S-EPS, LB-EPS and TB-EPS were also determined for each combined process at the optimum conditions.

2. Materials and methods

2.1. Physico-chemical characteristics of waste activated sludge

The WAS samples, obtained from a recirculation tank located after the aeration basin of an advanced municipal wastewater treatment plant in Istanbul, Turkey, were transferred to the laboratory as soon as sampling, then aerated for 1 h and preserved at 4 °C to maintain freshness. Characterization of the WAS samples is shown in Table 1.

2.2. Pretreatment procedure of WAS

The electrochemical setup of the pretreatment consisted of a batch reactor having a working volume of 500 mL, as shown in Fig. 1. Rectangular iron sheet electrodes in dimensions of 11.5 cm height, 6 cm width and 0.2 cm thickness were used as the cathode and the anode electrodes. The gap between the electrodes was kept at 2 cm, and they were connected to an ADC-3306D digital DC power supply to provide the desired current within the range of 1–5 A. The temperature values of the WAS varied between 25 and 60 °C with increasing applied current. Four oxidants (HP, CHC, PMS and PDS) were used in the EC

Table 1
Physico-chemical characteristics of raw WAS.

Parameter	Mean value	Standard deviation
Total solids (TS) (mg/L)	15,907	309.7
Total suspended solids (TSS) (mg/L)	14,625	912.2
Water content (%)	98.025	0.078
pH	7.05	0.04
Electrical conductivity (μS/cm)	1,900	84.8
Soluble COD (sCOD) (mg/L)	89.9	1.65
Total releasable COD (COD_{NaOH}) (mg/L)	6,975	271.5
Soluble TOC (mg/L)	14.2	0.3
Total releasable TOC (mg/L)	4,505	100.3
Soluble TN (mg/L)	20.6	0.4
Total releasable TN (mg/L)	293.3	5.7

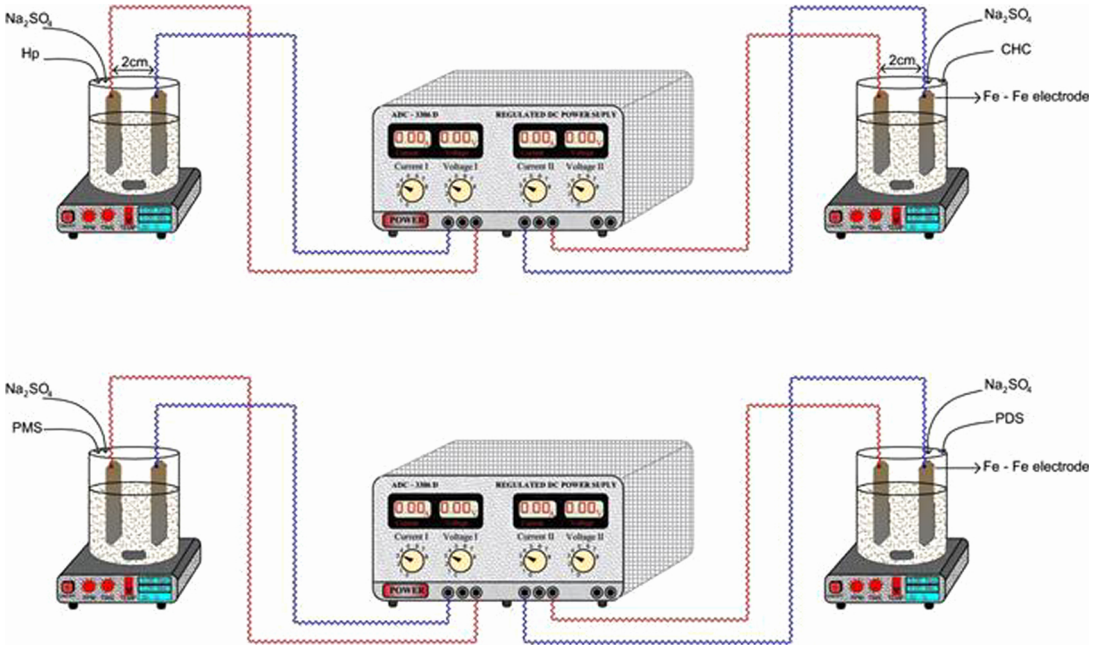


Fig. 1. The schematic diagram of this study.

process. 10 g/L of Na_2SO_4 was used as the supporting electrolyte solution in the treatment experiments (approximately 14 mS/cm of electrical conductivity). All experiments were performed in duplicates. The electrodes were washed with a sponge and then cleaned using hydrochloric acid solution (15 %) after each treatment test. All chemicals used in the study were of analytical-reagent grade.

2.3. Estimation of WAS disintegration degree

The disintegration degree (DD) of a sludge expresses the increment of soluble organic matters in released organic matter. Generally, sCOD, sTOC and sTN have been used to determine DD after pretreatment of WAS [33]. In this study, sCOD was used to evaluate the sludge disintegration performance in the EC process. Calculation of DD is shown in Eq. (7).

$$DD_{COD} = \left(\frac{COD_{S0} - COD_0}{COD_{NaOH} - COD_0}\right)*100 \quad (7)$$

Where, COD_0 and COD_{S0} are the concentrations of soluble COD (mg/L) for the raw and pretreated WAS by different oxidants by the EC process, respectively. COD_{NaOH} is the total releasable COD in the WAS (mg/L) after alkali hydrolysis (addition of 0.5 M NaOH at room temperature for 24 h). The raw and treated WAS were centrifuged at 4000 rpm and 4 °C for 30 min and then filtered using a 0.45-μm round filter to separate the soluble part of the sludge [41].

2.4. EPS extraction and analysis

Generally, soluble EPS (outer of flocs) (S-EPS), loosely-bound EPS (LB-EPS) and tightly-bound EPS (TB-EPS) have been determined as the three fractions of EPS in literature [34,43–45]. In this study, the EPS extraction procedures of the raw and pretreated WAS samples were performed based on studies by Liu et al. [34], Zhou et al. [46] and Xiao et al. [44] to extract S-EPS, LB-EPS and TB-EPS. 15 mL of the WAS sample was firstly centrifuged at 4000 × g at 4 °C for 15 min, and SB-EPS was obtained by collecting the supernatant. The WAS pellet left in the tube was then fully re-suspended by adding 15 mL of a sodium chloride (NaCl) solution (0.05 %). After this, the re-suspended sludge samples were sheared with applying vortex and incubated in a water bath (70 °C) for 1 min. The supernatant was collected as LB-EPS followed by second centrifugation at 4000 × g at 4 °C for 10 min. The residual pellet in the centrifuge tube was re-suspended to the initial volume by adding a 0.05 % NaCl solution and incubated in a water bath (60 °C) for 30 min. The sludge mixture was again centrifuged at 4000 × g at 4 °C for 15 min, and the supernatant was collected as TB-EPS. After the extractions, the protein and polysaccharide concentrations in SB-EPS, LB-EPS and TB-EPS were determined by the Lowry method and the phenol-sulfuric acid method, respectively [47,48].

2.5. Capillary suction time analysis

The WAS filterability was measured by CST analysis with a CST instrument (Triton) with standard CST filter paper using an 18-mm reservoir according to the Standard Methods [49]. The variation in filterability of WAS was determined by the reciprocal ratio of the pretreated sludge CST value to the raw WAS initial CST value (CST_0).

2.6. Other analytical and statistical analysis

COD, TSS and TS analyses of WAS were performed according to the Standard Methods [49]. TOC and TN concentrations were measured by a TOC/TN analyzer. The electrical conductivity and pH value of the raw and pretreated WAS were measured by a WTW Multiline P4 multimeter.

3. Results and discussion

3.1. Effects of oxidation dosage on the disintegration degree of WAS

According to previous WAS pretreatment studies, an increase in sCOD may be a good indicator to evaluate pretreatment effectiveness [50]. The applied current and oxidation time were set constant at 2.5 A and 30 min in the EC experiments. The WAS pH was kept at the original pH (7.05) in these experiments. Fig. 2 shows the effects of different oxidant dosages on the concentrations of sCOD and the values of DD_{COD}. When HP was added in the EC process, the maximum sCOD (531 mg/L) and DD_{COD} (6.40 %) values were found at the 0.5 mmol/g SS HP dosage (Fig. 2a). The increase of HP dosage after 0.5 mmol/g SS resulted in a dramatic decrease in sCOD and DD_{COD}. In EC combined with HP treatment, the obtained results showed that higher HP dosages

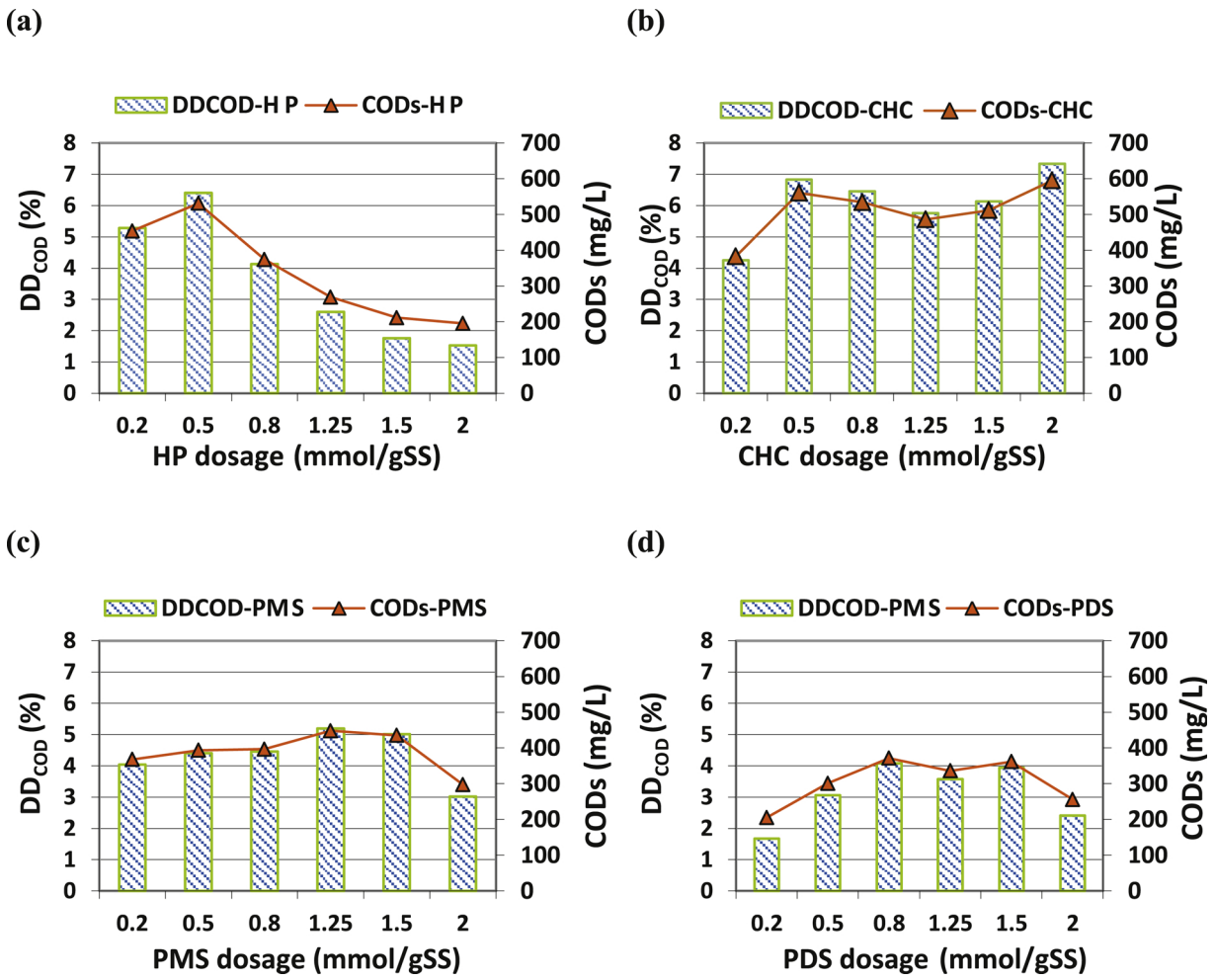


Fig. 2. Effect of oxidant dosage on DD_{COD} and CODs in electro-oxidation process (a) EC-HP combination; (b) EC − CHC combination; (c) EC-PMS combination; (d) EC-PDS combination (pH:7.05 (raw WAS pH); applied current:2.5 A, oxidation time 30 min).

inhibited DD due to the fact that an overdose of HP could scavenge ˙OH and result in elimination of ˙OH [51].

As shown in Fig. 2b, DD_{COD} and sCOD increased at 0.5 mmol/g SS, and then, the gradual decrease of these parameters was observed till 1.5 mmol CHC/g SS. Although the maximum DD_{COD} (7.33 %) and sCOD (595.2 mg/L) values were found at 2 mmol CHC/g SS, the optimum CHC dosage was selected 0.5 mmol CHC/g SS where the DD_{COD} and sCOD values were determined as 6.83 % and 560.6 mg/L.

In terms of sulfate radical-based electro-oxidation, lower DD_{COD} values were observed by EC with the PMS and PDS oxidants in comparison to the hydroxyl radical-based oxidants. The reason for these results could be due to slow direct reactions of PMS and PDS, and activation of these oxidants must be required by electrolysis, heat, UV, transition metal catalysis (for example Fe^{2+}, Ag^{2+}, Co^{2+}) or providing alkali conditions [33,52]. The Fe electrodes used in the EC experiments could ensure activation of PMS and PDS, but the DD_{COD} values were still found lower.

3.2. Effects of initial pH on the disintegration degree of WAS

Series of batch laboratory experiments were conducted to determine the effects of initial pH on release sCOD and DD_{COD} in the EC process using different oxidants (Fig. 3). The DD_{COD} values were found between 3.80%–4.45% at lower pH values between 2–6 in the EC process with HP, and an increase of pH values of the WAS led to an increase in the DD_{COD} value to 7.33 %. It was reported that low pH values led to Fe^{2+} charge neutralization and reduction of solubility due to dominated ferrous iron at the anode, and precipitation occurred, leading to WAS disintegration in the electrocoagulation (EC) process using iron electrodes [30]. It was also reported that higher pH values (>7) led to adsorption of inorganic and organic substances on amorphous hydroxide precipitates in the EC process [30]. On the other hand, EC with Fe electrodes by adding HP (called Electro-Fenton process) was more sensitive to pH change in comparison to the EC process.

In the EC − CHC treatment, the DD_{COD} values gradually increased with an increase in pH from 2 to 8, and the maximum DD_{COD} was found as 7.80 %. Increase of pH from 8 to 10 led to a decrease of DD_{COD} (Fig. 3b). Ye et al. [1] investigated EC combined with hypochlorite pretreatment of WAS, and pH was adjusted to 8 before the experiments. They achieved a significant increase in DD_{COD}, and the maximum DD_{COD} value was found as 30.4 % at the 0.8 % hypochlorite dosage, 40 min and 20 V by the combination of EC and ClO^- [1]. As shown in Fig. 3a-d, the maximum DD value was obtained in the combination of EC and CHC in these conditions (Applied current: 2.5 A, oxidation time: 30 min, dosage of HP and CHC: 0.5 mmol/g SS, PMS dosage: 1.25 mmol/g SS, PDS dosage: 0,8 mmol/g SS).

In EC combined with PMS and PDS treatment, the DD_{COD} values were obtained as 5.70 % and 6.31 % at pH 10, respectively. It may be stated that lower DD_{COD} values were found in EC combined PMS and PDS treatments in comparison to the hydroxyl-based oxidants.

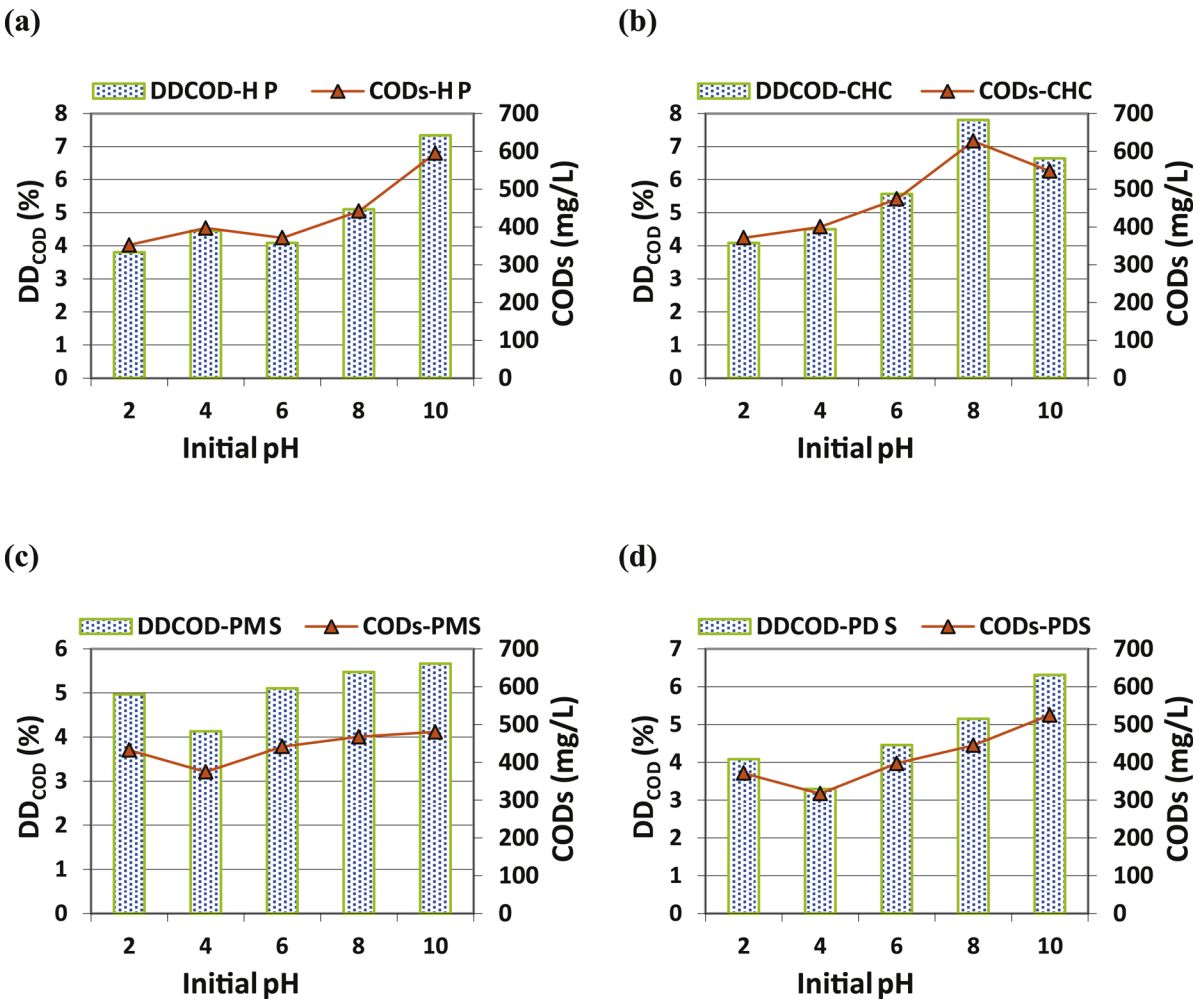


Fig. 3. Effect of initial pH on DD_{COD} and CODs in electro-oxidation process (applied current:2.5 A, oxidation time: 30 min), (a) EC-HP combination (HP dosage: 0.5 mmol/g SS); (b) EC − CHC combination, (CHC dosage: 0.5 mmol/g SS), (c) EC-PMS combination (PMS dosage: 1.25 mmol/g SS), (d) EC-PDS combination (PDS dosage: 0.8 mmol/g SS).

3.3. Effects of applied current

The effects of applied current on DD_{COD} were also investigated in the EC combined with HP, CHC, PMS and PDS treatments by a reaction time of 30 min. Batch experiments were conducted in different applied currents ranging from 1 A to 5 A (current density ranging from 14.5 mA/cm^2 to 72.5 mA/cm^2). The temperature of the samples varied between 26–58.5 °C when the applied current was increased. As seen in Fig. 4a-d, increasing the applied current resulted in increased sCOD and DD_{COD} in all combinations. The optimum applied current value was selected as 4 A (58 mA/cm^2) for the EC-HP, EC − CHC and EC-PDS combinations. The DD_{COD} values increased up to 4 A, and the values decreased for the EC − CHC and EC-PDS combinations. The decreasing DD_{COD} after the current of 4 A may be explained by strong oxidation effects of hydroxyl and sulfate radicals, whereas the optimum current value was chosen as 5 A (72.5 mA/cm^2) for EC combined with PMS treatment. The DD_{COD} values in these conditions were 11.6, 11.2, 9.8 and 8.9 % for the EC-HP, EC − CHC, EC-PMS and EC-PDS treatments, respectively.

Erden [41] investigated disintegration of waste sludge by an electro-oxidation process using Ti-Ti and Ti-Ti/RuO_2 electrode couples. The highest DD values were obtained as 13.9 % and 17.3 % at 20 V and 30 min of oxidation time for the Ti-Ti and Ti-Ti/RuO_2 electrodes, respectively. It was also reported that higher time and voltage led to a decrease in the DD values. Similar observations were reported by other authors that high voltage values caused mineralization of WAS preceding solubilization and led to a decrease in production of methane in anaerobic digestion [3,41].

3.4. Effects of oxidation time

Optimizing the oxidation time in EC combined with different oxidants is another important factor. Fig. 5a-d shows the variations of sCOD and DD_{COD} with oxidation time. In the EC-HP combination, the sCOD concentrations and DD_{COD} values slightly increased with increasing electrolysis time up to 45 min, and then, the sCOD and DD_{COD} values reached a plateau (approximately 900 mg/L and 11.75 %, respectively) (Fig. 5a). The sCOD and DD_{COD} values increased up to 45 min of reaction time, and then, decreased after this time in the EC − CHC treatment. A similar observation was reported by Erden [41] as the sludge disintegration decreased with higher time of application. In comparison to the EC-HP treatment, a lower DD_{COD} value was found (11.10 %) at 45 min in the EC − CHC combination (Fig. 5b).

DD_{COD} enhanced from 6.92 to 9.48 % with an increase in the oxidation time from 15 to 30 min, and it slightly increased from 9.48 % to 9.61 % with an increase in time from 30 to 60 min in the EC-PMS treatment. The optimum oxidation time was chosen as 30 min for its economical aspect, although the maximum DD_{COD} value (10.07 %) was

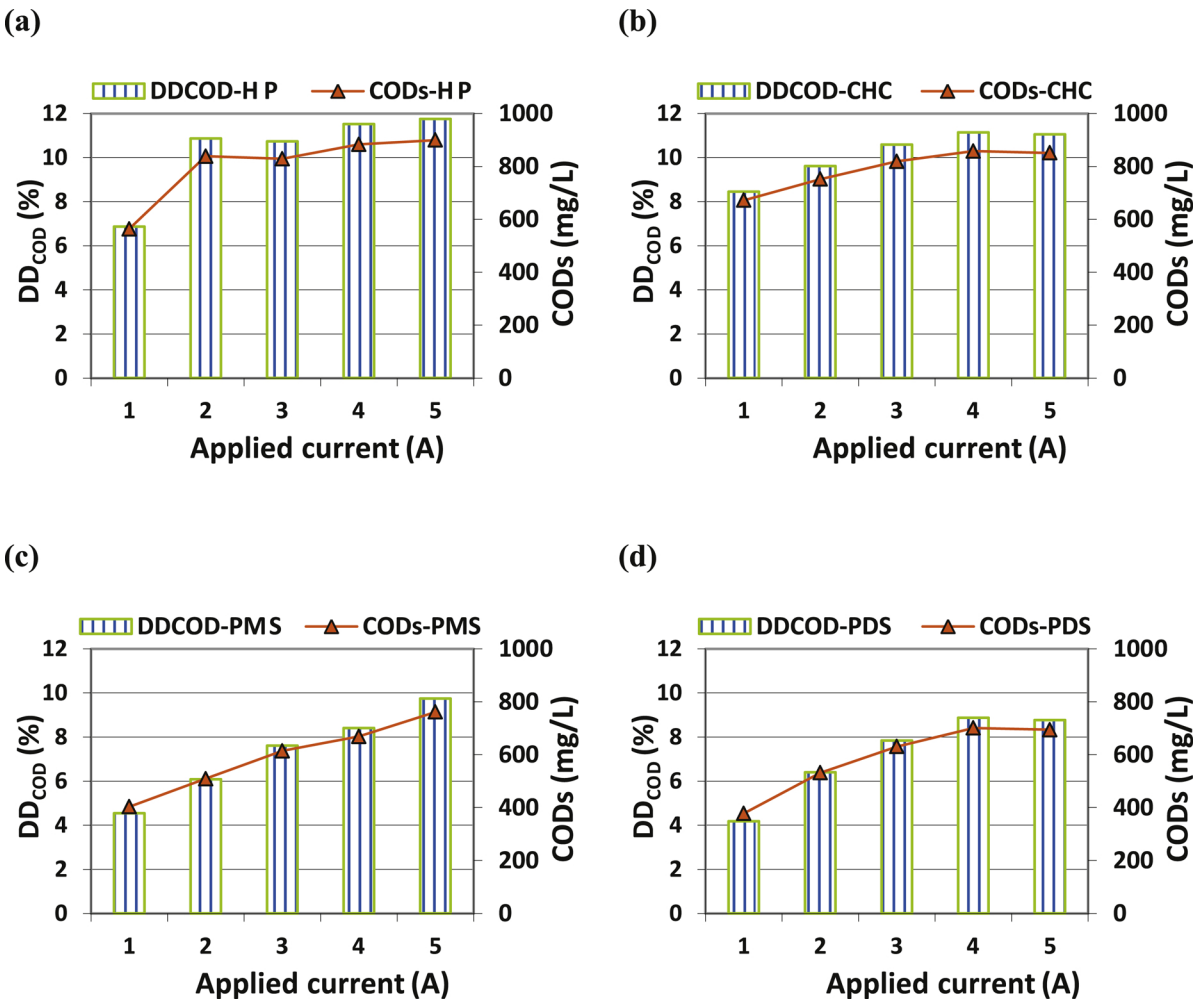


Fig. 4. Effect of applied current on DD_{COD} and CODs in electro-oxidation process; (a) EC-HP combination; (b) EC − CHC combination; (c) EC-PMS combination; (d) EC-PDS.combination (Oxidation time: 30 min, pH: 10 for EC combined with HP, PMS and PDS treatment, pH: 8 for CHC treatment).

found at 90 min of oxidation time in the EC-PMS combination. In the EC-PDS treatment, the DD_{COD} value increased gradually from 6.73 % to 10.54 %, when the oxidation time increased from 15 min to 45 min. After this oxidation time, DD_{COD} increased slightly from 10.54 % to 11.28 % with an increase of time from 45 min to 90 min. Therefore, the optimum time was selected as 45 min for the EC-PDS treatment.

According to the obtained results, the DD_{COD} values were determined in the following order; EC-HP (11.75 % at 45 min) > EC − CHC (11.10 % at 45 min) > EC-PDS (10.54 % at 45 min) > EC-PMS (9.48 % at45 min) under the optimized conditions.

3.5. Effects of electrolyte solution concentration

In this study, 10 g/L of Na_2SO_4 was used as the supporting electrolyte solution in the previous experiments. Different concentrations of Na_2SO_4 (between 5–20 g/L) were investigated in each treatment as the concentration of the electrolyte solution is another significant factor in sludge electro-disintegration. Fig. 6a-d shows the variations in the sCOD and DD_{COD} values with different Na_2SO_4 concentrations. As seen in Fig. 6a, the DD_{COD} values increased from 7.60 % to 11.80 % when the concentration of Na_2SO_4 was increased from 5 to 10 g/L, and a slightly increased of DD_{COD} value was observed with an increase of Na_2SO_4 from 10 to 15 g/L in EC combined with HP treatment. Additional increase of Na_2SO_4 did not enhance the DD_{COD} value, which was found as 9.80 % at 20 g/L in the EC-HP treatment. On the other hand, the maximum DD_{COD} value was obtained as 11.11 % at the 10 g/L Na_2SO_4 concentration, and lower and higher concentrations of Na_2SO_4 did not enhance the DD_{COD} of WAS in the EC − CHC treatment (Fig. 6b).

The DD_{COD} values of WAS did not significantly change with an increase in Na_2SO_4 concentrations (between and 9.37 and 9.78 %); therefore, the optimum Na_2SO_4 concentration was chosen as 10 g/L in EC combined with PMS treatment in which the DD_{COD} value was found as 9.61 %. On the other hand, the Na_2SO_4 concentration in the EC-PDS treatment was significantly effective on the DD_{COD} of WAS, and the maximum DD_{COD} value was obtained as 10.65 % at the 10 g/L Na_2SO_4 concentration. Lower and higher concentrations of Na_2SO_4 were determined to have an adverse effect on the DD_{COD} value of WAS in the EC-PDS treatment.

To sum up the obtained result, the DD_{COD} values were determined in the following order: EC-HP (11.80 %) > EC − CHC (11.11 %) > EC-PDS (10.65 %) > EC-PMS (9.61 %) under the optimized conditions.

3.6. Disintegration degree in terms of soluble COD, TN and TOC at the optimum conditions

During the EC pretreatment combined with different oxidants, the DD values were measured in TOC (DD_{TOC}) and TN (DD_{TN}) at the optimum conditions. Fig. 7 shows the effect of each oxidant on the sCOD, TOC and TN concentrations of WAS at the optimized conditions in the combined processes. As shown in Fig. 7, the DD_{TOC} values for each pretreatment were found lower than the DD_{COD} values at the optimized conditions as the DD_{TOC} values were 11.76 %, 8.4 %, 5.8 % and 5.7 %

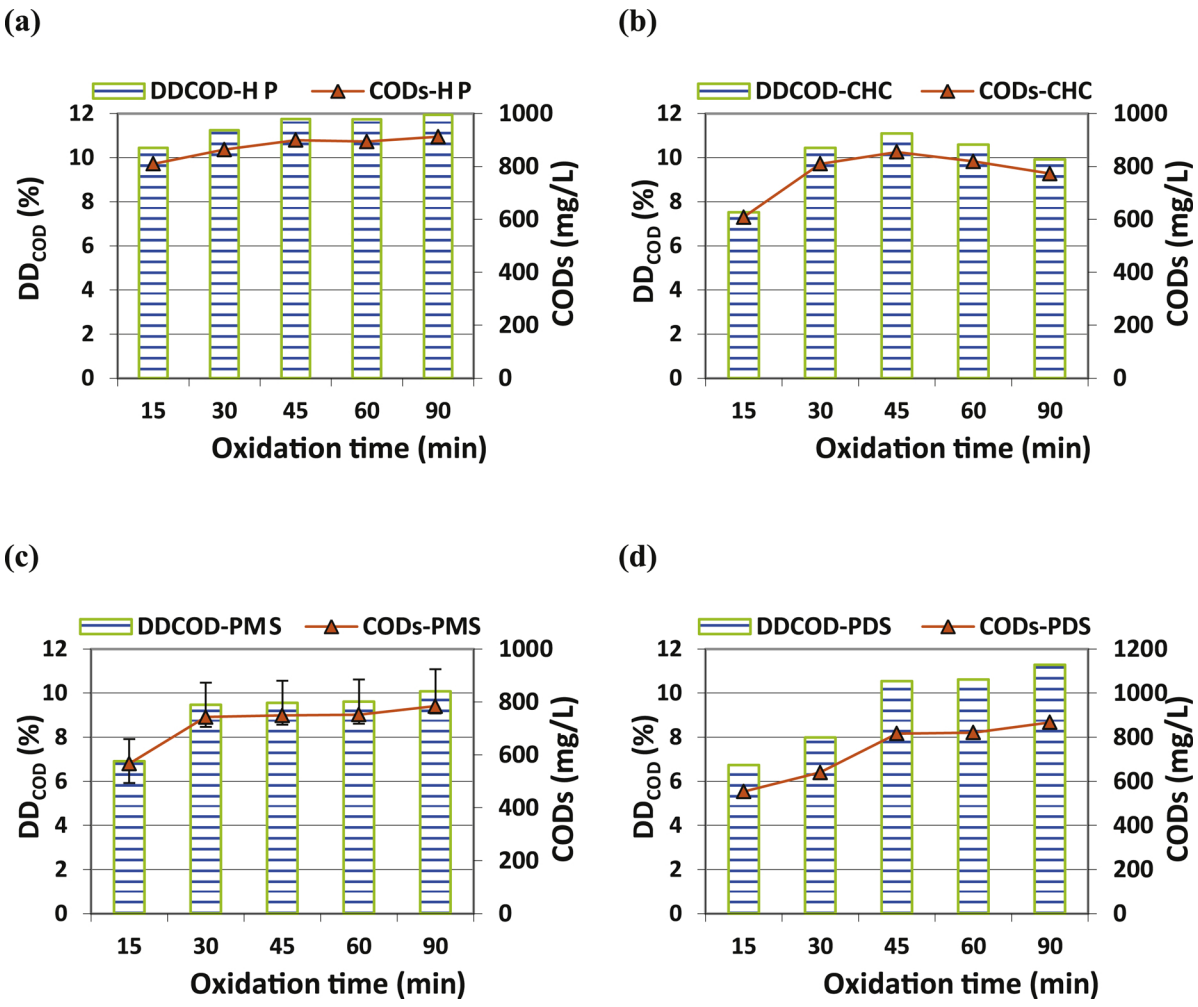


Fig. 5. Effect of oxidation time on DD_{COD} and CODs in electro-oxidation process; (a) EC-HP combination; (B) EC − CHC combination; (c) EC-PMS combination; (d) EC-PDS combination (Oxidation time: 30 min, applied current: 4 A for EC combined with HP, CHC and PDS treatment, 5 A for PMS treatment).

respectively for the EC-HP, EC − CHC, EC-PMS and EC-PDS treatments. The EC-HP co-treatment was the most effective treatment in terms of DD_{TOC} like DD_{COD}, and the TOC concentration increased 38.72-fold after disintegration. The other co-treatments did not increase the concentration of TOC as much as the EC-HP co-treatment. On the other hand, the DD_{TN} values were found almost equivalent to the DD_{COD} values for all treatment except for the EC − CHC treatment. In terms of the DD_{TN} values, the most effective process was the EC-PDS co-treatment, and the TN concentration increased 2.45-fold after disintegration.

When the obtained results were compared to previous study performed by Ren et al. [33], it is observed that lower DD_{TOC} and DD_{TN} values were found in this study. Ren et al. [33] reported that the DD_{TOC} and DD_{TN} values of WAS were found 50 % higher in comparison to the DD_{COD} values at the dosage of 12 mgPMS/g SS in PMS pretreatment.

3.7. Reduction of CST of disintegrated WAS at the optimum conditions

The variation in disintegrated WAS filterability was determined by the reciprocal ratio of the CST value of disintegrated sludge to the initial CST value of the raw sludge (CST_0). A lower ratio of CST/CST_0 indicates an increase in WAS filterability. The standardized CST values are presented in Fig. 8. The CST value of the raw sludge was determined as 13.1 ± 0.43 s, and the CST/CST_0 ratios of the disintegrated WAS were 1.38, 0.73, 0.71 and 0.64 for the EC-HP, EC − CHC, EC-PMS and EC-PDS treatments, respectively. In other words, CST values of the WAS decreased by 27.34 %, 29.25 % and 36.14 %, respectively, after the treatment at the optimum conditions for the combinations EC − CHC, EC-PMS and EC-PDS. The EC-HP treatment combination did not enhance WAS filterability as the treated CST value was found as 18.1 ± 1.13 s. As shown in Fig. 8, filterability levels of WAS were determined in the following order: EC-PDS > EC-PMS > EC − CHC > EC-HP under the optimum conditions.

3.8. EPS concentration and type of raw and pretreated WAS

Some of the main components of mixed liquor are EPSs whose main fractions are generally PN and PS. Therefore, the dewaterability of WAS is mainly affected by the PN and PS fractions of EPSs [53,54]. The polysaccharide and protein concentrations of EPSs of raw and disintegrated WAS are shown in Fig. 9. The protein concentrations of S-EPS, LB-EPS and TB-EPS of the raw WAS were determined as 29 mg/L, 11.2 mg/L and 31.45 mg/L, respectively. The polysaccharide concentrations of the raw WAS were found as 13 mg/L, 25.4 mg/L and 24.5 mg/L respectively for S-EPS, LB-EPS and TB-EPS. As shown in Fig. 9a, the polysaccharide and protein concentrations of S-EPS increased after all combined disintegration processes. It was noted that the higher fractions of S-EPS were found as protein for the raw and disintegrated sludge samples.

The protein concentrations of LB-EPS slightly decreased from 11.2 to 10.9 mg/L, 8.1 and 9.7 mg/L for the respective combinations of EC − CHC, EC-PMS and EC-PDS, while the protein concentrations of LB-

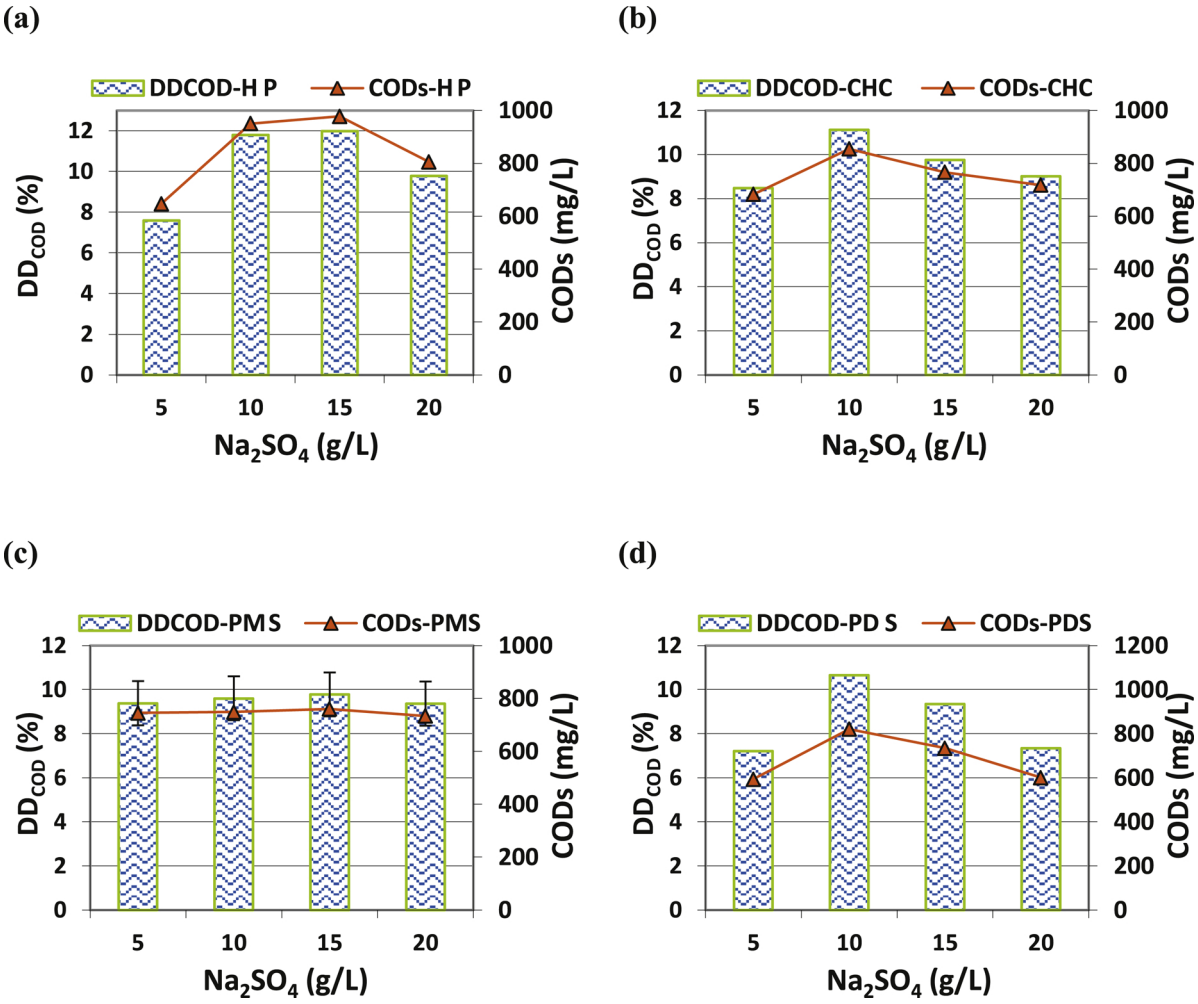


Fig. 6. Effect of electrolyte concentration on DD_{COD} and CODs in electro-oxidation process; (a) EC-HP combination; (B) EC – CHC combination; (c) EC-PMS combination; (d) EC-PDS combination (Oxidation time: 30 min for PMS treatment, 45 min for EC combined with HP, CHC and PDS treatment).

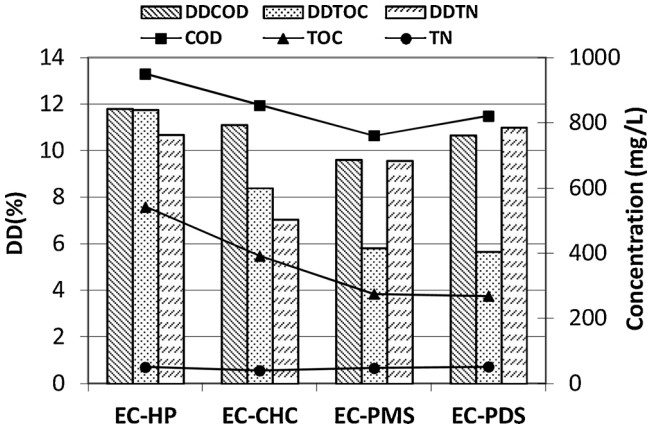


Fig. 7. DD of WAS in terms of the concentrations of COD, TOC and TN under the optimized conditions in EC combined with HP, CHC, PMS and PDS treatment.

EPS increased by 64 % for the EC-HP treatment compared to the LB-EPS of the raw WAS. Moreover, the polysaccharide concentrations of LB-EPS of the disintegrated sludge decreased from 25.4 mg/L to 10.4, 7.6, 5.4 and 6.4 mg/L after the EC-assisted HP, CHC, PMS and PDS treatments, respectively. The total LB-EPS concentrations of the disintegrated sludge decreased by 3%, 49.5 %, 62 % and 13 % for respectively the EC-HP, EC – CHC, EC-PMS and EC-PDS treatments. In terms of the TB-EPS concentrations, all fractions of TB-EPS significantly decreased after the EC process combined with the hydroxyl and sulfate radical-based oxidants. These observations showed that the EC-assisted HP, CHC, PMS and PDS treatments disintegrated the flocs of WAS and converted the TB-EPS and LB-EPS to S-EPS. It was found in several studies that TB-EPS was converted to S-EPS and LB-EPS by disruption and disintegration of WAS flocs [44,55,56]. Additionally, the protein fraction of S-EPS, LB-EPS and TB-EPS was found higher in comparison to polysaccharide after all treatment combinations (Fig. 9a-c). The protein predominance of the EPSs in the WAS could be the result of large quantities of exoenzymes in WAS flocs [57].

Furthermore, the total LB-EPS decreased by 3%, 49.45 %, 63.11 % and 56.01 % for the EC-HP, EC – CHC, EC-PMS and EC-PDS treatments, respectively. The TB-EPS concentrations decreased respectively by 80.33 %, 77.92 %, 84.82 % and 78.73 %. The obtained results showed that the effects of combined treatment on the removal of TB-EPS were higher than LB-EPS. Liao et al. [58] reported that the TB-EPS layer is the closest layer to the microorganism, and the surface of the bacteria has negative charges. When Fe^{2+} ions were solubilized to the WAS, they were absorbed by the negative surface of the microbial community, and Fenton's reaction happened near the organism where TB-EPS was located. Therefore, TB-EPS decreased more than LB-EPS. Similar results were obtained by Masihi et al. [42].

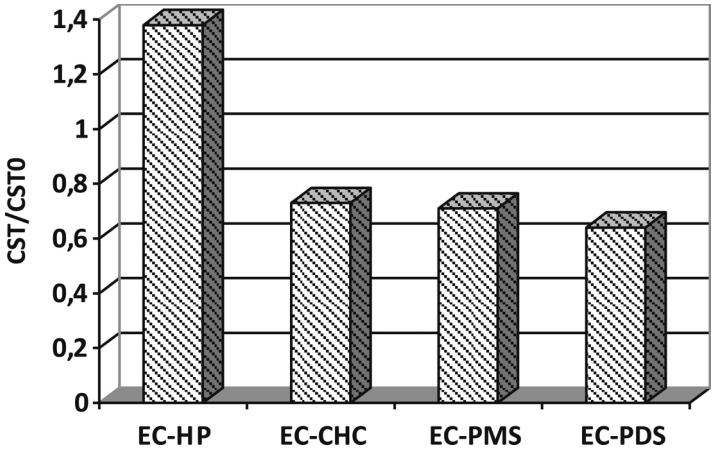


Fig. 8. Relative CST values of disintegrated sludge samples.

3.9. Comparison of the obtained results to other studies

There are several pre-treatment studies with electrochemical oxidation in the literature. However, the authors were not able to find a comparative study to investigate the EC-assisted disintegration process using the HP, CHC, PMS and PDS oxidants. To the best of our knowledge, this is the first study in the literature using the EC treatment combined with HP, CHC, PMS and PDS to enhance the disintegration of WAS. Song et al. [38] investigated enhancement of WAS solubilization by electrochemical pre-treatment using a pair of RuO_2/Ti mesh plate electrodes, and they determined the effect of operational parameters on VS and VSS removal efficiencies and sCOD. It was found that the sCOD concentration increased from 36 − 52 mg/L to 348 mg/L after the electrochemical pre-treatment at the 12.9 g/L sludge concentration, 30 min electrolysis time, pH 10 and 5 W electrical power (the DD_{COD} value was calculated to be between 1.56 % and 1.79 %). Chen et al. [39] researched the physical and chemical characteristics of WAS treated with electrical field using a Ti/IrO_2 anode and a Ti cathode. In the study, the sCOD values increased by 92.11 %, 132.34 % and 195.9 % after the 30 min treatment at 2 V/cm, 4 V/cm and 6 V/cm, respectively. The maximum sCOD/TCOD values were found to be approximately 8%, 9.5 % and 11.5 % at these operational parameters. The authors reported that increases in the sCOD values could be explained by disruption of the WAS floc structure, and these floc disruptions may have led to a release of extracellular and intracellular polymeric materials, such as proteins and polysaccharides. It was also reported in the study that the higher supplied power could increase the solubilization of WAS due to the decomposition of organic matter. Gharibi et al. [40] investigated a bipolar electrolysis/electrocoagulation (EL/EC) reactor using two series of Ti/RuO_2 plates to enhance sludge dewaterability, and the DD value was found as 2.5 % at an electrolysis time of 20 min and a voltage of 30 V. The maximum CST and SRF reduction values were also observed at these conditions. They reported that the increased DD_{SCOD} values led to increasing reduction of CST and SRF values due to the disruption of the WAS flocs. In the study, the simultaneous application of EL and EC was found to be effective in enhancing WAS dewaterability, as EC helps achieve a higher DD_{SCOD} while maintaining the desired dewaterability of sludge. Pérez-Rodríguez et al. [4] investigated the influence of some operating conditions on the solubilization of organic matter of WAS by electrochemical treatment using boron-doped diamond on silicon substrate electrodes. It was determined that the maximum degree of solubilization was 1.78 % at the 30 min electrooxidation time, 19.3 mA/cm^2 current density and 3.8 L/min flow rate.

Fard et al. [30] studied reduction of MBR excess sludge by the combination of EC and electro-Fenton (EF) oxidation processes. In the study, Fe-Fe electrode pairs were used, and the current and voltage (50 V) were kept constant. In the study, the sCOD value was found as 1490 mg/L after 70 min of EC time, whereas the maximum concentration of sCOD was found as 2500 mg/L after 50 min of EF time at 7000 mg/L HP dosage, 41.7 A/m^2, pH 3. Additionally, Ye et al. [1] investigated EC combined with hypochlorite (ClO^-) pretreatment for improving disintegration of WAS, and they found that the ClO^- dosage had a significant effect on WAS solubilization. In the study, Ti/RuO_2 meshes were used as the anode and the cathode, the experiments were conducted at 20 V of applied voltage, 40 min of time and pH 8.0, and the optimum ClO- dosage was determined as 0.8 % (V/V) in which the DD_{COD} value was found as 30.2 %. In these ClO- dosages, protein and polysaccharide concentration increased, respectively, by 10.3 and 6.1 times higher than that of raw sludge. It was reported that hydrolytic bacteria and/or acidogenic microorganisms could readily used these released protein and polysaccharide constituents, and thus, the hydrolysis stage of the anaerobic digestion process could accelerate [1]. Ye et al. [7] also investigated electrochemical pretreatment of WAS using two Ti/RuO_2 mesh plate electrodes and a glass cell, and they obtained disintegration degrees between 9.02 % and 9.72 % at 30 min of reaction time, 20 V of electrolysis voltage and 5-cm electrode distance. They also investigated the concentration of soluble protein and polysaccharide after EC pretreatment, and they found an increase in proteins from 40.60 mg/L to 122.47 mg/L and in polysaccharides from 29.91 mg/L to 50.37 mg/L. Yu et al. [10] examined electrochemical pretreatment of WAS using Ti/RuO_2 mesh plate electrodes and adding sodium hypochlorite by 0.6 % (V/V). 38.3 % COD solubilization was found at the electrolysis voltage of 20 V, electrolysis time of 40 min and electrode spacing of 2 cm. These pretreatments ensured the highest cumulative biogas production (647 L/kgVS) in comparison to other treatment methods such as thermal pretreatment, thermal alkaline pretreatment and alkaline pretreatment. Disintegration of biological WAS by an electro-oxidation process with a pair of Ti/RuO_2 and Ti electrodes was investigated by Erden et al. [41]. The optimal conditions were found as 20 V for 30 min for both electrode couples. The DD_{COD} values were found as 13.9 % for Ti electrode application, and addition of 10 g/L Na_2SO_4 supporting electrolyte increased the DD_{COD} value from 13.9%–17.3%. Ti/RuO_2 electrodes provided higher DD values, and the highest DD_{COD} values were determined as 20.4 % and 16.6 %, respectively, when adding and not adding the Na_2SO_4 solution. Chen et al. [29] investigated WAS pretreatment by electro-Fenton (EF) oxidation for improving WAS dewatering and disintegration. In the study, RuO_2-coated titanium and active carbon fiber were used as the anode and the cathode, respectively. 50 mmol/L Na_2SO_4 and 50 mmol/L Fe^{2+} were added into the EF reactor, and air bubbles were supplied with an air pump at 3 L/min for HP generation. The authors found that the EF process could improve the WAS sedimentation capacity by 35.97 %, and the sCOD concentration increased from 136.5 mg/L to 934.6 mg/L

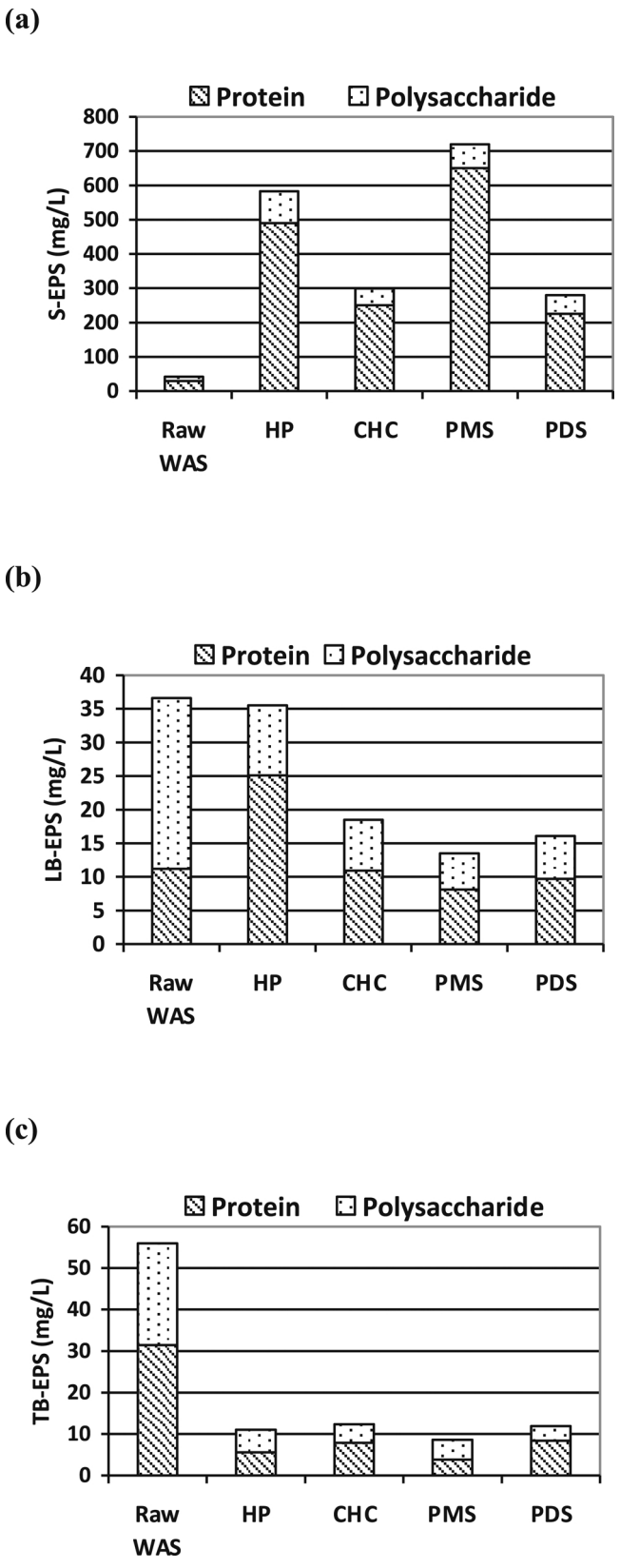


Fig. 9. The concentration of protein and polysaccharide in S-EPS (a), LB-EPS (b) and TB-EPS (c) under optimum conditions.

after the EF treatment. The authors also found a negative relationship between the SRF and sCOD values, which indicated that disintegration of WAS contributed to improvement of dewaterability. It was reported in the study that the EF process could also reduce floc sizes and zeta potential values in the negative direction of WAS. These results clearly showed that the EF process provoked the disintegration of large flocs

into smaller ones, and dewatering of WAS could be enhanced when the zeta potential of the WAS particles was closer to zero.

In terms of sludge dewaterability by electrochemical pretreatment methods, several studies have been performed by researchers [36,42,59]. An electrochemical-Fenton process was investigated by Masihi and Gholikandi [42] for the aim of conditioning and dewatering of anaerobically digested sludge samples. It was found that the SRF values decreased by 14.5 % and 93.8 % for the electrochemical (optimum conditions: electrolysis voltage 11 V, time 20 min) and electrochemical-Fenton (optimum conditions: Fe^{2+} 15 g/g dry solid (DS), H_2O_2 25 g/g DS, electrolysis voltage 11 V, time 20 min treatment) processes. Time to filter (TFF) values were also reduced by 9.8 % and 75.9 % respectively for the electrochemical and electrochemical-Fenton treatments. It was reported that the TB-EPS and LB-EPS values were reduced by the electrochemical-Fenton process, whereas the S-EPS value increased as it was expected. Xiao et al. [59] also investigated municipal sludge dewaterability by electrochemical pretreatment. In the study, the effects of several electrolytes (NaCl, Na_2SO_4, $NaNO_3$, and $NaClO_4$) on electrolysis pretreatment of WAS using Ti/PbO_2 electrodes were examined. A higher WAS dewaterability value was found by using a NaCl solution as it formed a large amount of active chlorine species, which oxidized the WAS cells to improve sludge dewaterability. On the other hand, sludge dewaterability by electrolysis/electrocoagulation combined with zero valent iron activated persulfate processes was investigated by Li et al. [36] using a Ti/RuO_2-IrO_2 anode and a Ti mesh cathode. The four iron electrodes which were used as the induced electrode array for electrocoagulation were placed in the center of the anode and the cathode. The SRF and CST values of the WAS decreased respectively by 84.4 % and 49.1 % after the treatment at the optimum dewatering conditions (40 V voltage and 4.15 g/L $Na_2S_2O_8$). The authors reported that the electrolysis/electrocoagulation combined with zero valent iron activated persulfate process significantly disrupted the EPS and degraded the protein contents. It was also reported in the study that viscosity and negative zeta potential of the WAS decreased, the bound water inside the EPS and cells was released, and thus, sludge dewaterability improved [36].

In this study, the obtained results were in agreement with the aforementioned studies in that the DD of the WAS could be enhanced by the electrochemical oxidation processes. Therefore, electrochemical oxidation processes could be used as a pretreatment of WAS to accelerate the hydrolysis stage of the anaerobic sludge digestion process. Electrochemical oxidation processes could also improve WAS dewaterability as the intracellular protein and polysaccharide concentrations of the WAS particles decreased in shorter treatment times after these treatment methods. It is known that the contents of EPS are important, as the influence of protein is more than polysaccharides on sludge dewatering [42,60,61]. The free radical of $^{\cdot}OH$ or $^{\cdot}SO_4^{2-}$ could react with the organic materials of microorganism cells, resulting in degradation of EPS, disruption of microbial cell membrane and release of intracellular organic materials into the filtrate in electrochemical oxidation processes of WAS. Thus, sludge disintegration and dewaterability could be enhanced after these pretreatments.

4. Conclusion

The main objective of this study was to determine the performance of EC treatments combined with several hydroxyl (HP and CHC) and sulfate (PMS and PDS) radical-based oxidants in enhancing sludge disintegration as measured by released sCOD. In this context, the oxidant dosages, initial pH, applied current, electrolysis time and electrolyte solution concentration, which are important parameters that affect WAS disintegration, were optimized in batch experiments. The maximum DD_{COD} values were found as 11.80 %, 11.11 %, 9.61 % and 10.65 %, respectively, for EC combined with HP, CHC, PMS and PDS at the optimized conditions. In terms of the released TOC and TN concentrations, the DD_{TOC} values of 11.76 %, 8.4 %, 5.8 % and 5.7 % were achieved respectively for the EC-HP, EC − CHC, EC-PMS and EC-PDS treatments. Moreover, the DD_{TN} values were found almost equivalent to the DD_{COD} values for all treatments except for the EC − CHC treatment. Under these operational conditions, the CST values were reduced by 27.34 %, 29.25 % and 36.13 % for EC combined with the CHC, PMS and PDS treatments, respectively. The EC-HP treatment did not enhance WAS filterability as the treated CST values increased from 13.1 s of the raw sludge to 18.1 s of the treated sludge. EC treatment combined with the oxidants increased the S-EPS concentrations, especially the protein fraction, whereas the LB-EPS concentration decreased by between 3% and 63.11 %. Additionally, the TB-EPS concentrations decreased by 77.92 %–84.82 % for all treatments. The obtained results indicated that the effect of the EC treatment combined with the oxidants on the removal of TB-EPS was more significant than it was for that of LB-EPS. It was noted that the protein fractions of the EPS for all treatments were found higher than the polysaccharide concentration, especially for the EC-HP combination, and the protein fractions of the EPS could mainly affect sludge dewaterability.

CRediT authorship contribution statement

Hanife Sari Erkan: Conceptualization, Investigation, Writing - original draft. **Guleda Onkal Engin:** Resources, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] C. Ye, H. Yuan, Z. Lou, N. Zhu, Combined electrochemical and hypochlorite pretreatment for improving solubilization and anaerobic digestion of waste-activated sludge: effect of hypochlorite dosage, Energy Fuels 30 (2016) 2990–2996.
[2] Q. Xu, X. Li, R. Ding, D. Wang, Y. Liu, Q. Wang, J. Zhao, F. Chen, G. Zeng, Q. Yang, Understanding and mitigating the toxicity of cadmium to the anaerobic fermentation of waste activated sludge, Water Res. 124 (2017) 269–279.
[3] G. Zhang, J. Yang, H. Liu, J. Zhang, Sludge ozonation: disintegration, supernatant changes and mechanisms, Bioresour. Technol. 100 (2009) 1505–1509.
[4] M. Pérez-Rodríguez, A. Cano, U. Durán, J. Barrios, Solubilization of organic matter by electrochemical treatment of sludge: influence of operating conditions, J. Environ. Manage. 236 (2019) 317–322.
[5] M. Seggiani, S. Vitolo, M. Puccini, A. Bellini, Cogasification of sewage sludge in an updraft gasifier, Fuel 93 (2012) 486–491.
[6] B. Yu, J. Xu, H. Yuan, Z. Lou, J. Lin, N. Zhu, Enhancement of anaerobic digestion of waste activated sludge by electrochemical pretreatment, Fuel 130 (2014) 279–285.
[7] C. Ye, H. Yuan, X. Dai, Z. Lou, N. Zhu, Electrochemical pretreatment of waste activated sludge: effect of process conditions on sludge disintegration degree and methane production, Environ. Technol. 37 (2016) 2935–2944.
[8] S. Kavitha, C. Jayashree, S.A. Kumar, I.T. Yeom, J.R. Banu, The enhancement of anaerobic biodegradability of waste activated sludge by surfactant mediated biological pretreatment, Bioresour. Technol. 168 (2014) 159–166.
[9] Y. Feng, Y. Zhang, X. Quan, S. Chen, Enhanced anaerobic digestion of waste activated sludge digestion by the addition of zero valent iron, Water Res. 52 (2014) 242–250.
[10] L. Leng, X. Yuan, H. Huang, H. Jiang, X. Chen, G. Zeng, The migration and transformation behavior of heavy metals during the liquefaction process of sewage sludge, Bioresour. Technol. 167 (2014) 144–150.
[11] L. Appels, S. Houtmeyers, J. Degrève, J. Van Impe, R. Dewil, Influence of microwave pre-treatment on sludge solubilization and pilot scale semi-continuous anaerobic digestion, Bioresour. Technol. 128 (2013) 598–603.
[12] C. Chu, D. Lee, B.-V. Chang, C. You, J. Tay, "Weak" ultrasonic pre-treatment on anaerobic digestion of flocculated activated biosolids, Water Res. 36 (2002) 2681–2688.
[13] G. Erden, A. Filibeli, Ozone oxidation of biological sludge: effects on disintegration,

anaerobic biodegradability, and filterability, Environ. Prog. Sustain. Energy 30 (2011) 377–383.
[14] I. Yeom, K. Lee, Y. Lee, K. Ahn, S. Lee, Effects of ozone treatment on the biodegradability of sludge from municipal wastewater treatment plants, Water Sci. Technol. 46 (2002) 421–425.
[15] D. Zhang, Y. Chen, Y. Zhao, X. Zhu, New sludge pretreatment method to improve methane production in waste activated sludge digestion, Environ. Sci. Technol. 44 (2010) 4802–4808.
[16] D. Devlin, S. Esteves, R. Dinsdale, A. Guwy, The effect of acid pretreatment on the anaerobic digestion and dewatering of waste activated sludge, Bioresour. Technol. 102 (2011) 4076–4082.
[17] G. Burger, W. Parker, Investigation of the impacts of thermal pretreatment on waste activated sludge and development of a pretreatment model, Water Res. 47 (2013) 5245–5256.
[18] C. Bougrier, J.P. Delgenès, H. Carrère, Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion, Chem. Eng. J. 139 (2008) 236–244.
[19] M. Barjenbruch, O. Kopplow, Enzymatic, mechanical and thermal pre-treatment of surplus sludge, Adv. Environ. Res. 7 (2003) 715–720.
[20] H. Ge, P.D. Jensen, D.J. Batstone, Pre-treatment mechanisms during thermophilic–mesophilic temperature phased anaerobic digestion of primary sludge, Water Res. 44 (2010) 123–130.
[21] V.G. Sharmila, S. Kavitha, K. Rajashankar, I.T. Yeom, J.R. Banu, Effects of titanium dioxide mediated dairy waste activated sludge deflocculation on the efficiency of bacterial disintegration and cost of sludge management, Bioresour. Technol. 197 (2015) 64–71.
[22] M. Anjum, H.A. Al-Talhi, S.A. Mohamed, R. Kumar, M. Barakat, Visible light photocatalytic disintegration of waste activated sludge for enhancing biogas production, J. Environ. Manage. 216 (2018) 120–127.
[23] E. Feki, S. Khoufi, S. Loukil, S. Sayadi, Improvement of anaerobic digestion of waste-activated sludge by using H 2 O 2 oxidation, electrolysis, electro-oxidation and thermo-alkaline pretreatments, Environ. Sci. Pollut. Res. 22 (2015) 14717–14726.
[24] Q. Wang, G. Jiang, L. Ye, Z. Yuan, Enhancing methane production from waste activated sludge using combined free nitrous acid and heat pre-treatment, Water Res. 63 (2014) 71–80.
[25] S. Behera, R. Arora, N. Nandhagopal, S. Kumar, Importance of chemical pretreatment for bioconversion of lignocellulosic biomass, Renewable Sustain. Energy Rev. 36 (2014) 91–106.
[26] G. Divyapriya, I.M. Nambi, J. Senthilnathan, An innate quinone functionalized electrochemically exfoliated graphene/Fe3O4 composite electrode for the continuous generation of reactive oxygen species, Chem. Eng. J. 316 (2017) 964–977.
[27] H. Li, Y. Wang, H. Zheng, Variations of moisture and organics in activated sludge during Fe0/S2O82− conditioning–horizontal electro-dewatering process, Water Res. 129 (2018) 83–93.
[28] E.J. Rosenfeldt, K.G. Linden, S. Canonica, U. Von Gunten, Comparison of the efficiency of OH radical formation during ozonation and the advanced oxidation processes O3/H2O2 and UV/H2O2, Water Res. 40 (2006) 3695–3704.
[29] Y. Chen, H. Chen, J. Li, L. Xiao, Rapid and efficient activated sludge treatment by electro-Fenton oxidation, Water Res. 152 (2019) 181–190.
[30] M.A. Fard, B. Aminzadeh, M. Taheri, S. Farhadi, M. Maghsoodi, MBR excess sludge reduction by combination of electrocoagulation and Fenton oxidation processes, Sep. Purif. Technol. 120 (2013) 378–385.
[31] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100 (2003) 475–502.
[32] X. Zhu, Q. Yang, X. Li, Y. Zhong, Y. Wu, L. Hou, J. Wei, W. Zhang, Y. Liu, C. Chen, Enhanced dewaterability of waste activated sludge with Fe (II)-activated hypochlorite treatment, Environ. Sci. Pollut. Res. 25 (2018) 27628–27638.
[33] W. Ren, Z. Zhou, Y. Zhu, L.-M. Jiang, H. Wei, T. Niu, P. Fu, Z. Qiu, Effect of sulfate radical oxidation on disintegration of waste activated sludge, Int. Biodeterior. Biodegradation 104 (2015) 384–390.
[34] J. Liu, Q. Yang, D. Wang, X. Li, Y. Zhong, X. Li, Y. Deng, L. Wang, K. Yi, G. Zeng, Enhanced dewaterability of waste activated sludge by Fe (II)-activated peroxymonosulfate oxidation, Bioresour. Technol. 206 (2016) 134–140.
[35] G.-Y. Zhen, X.-Q. Lu, Y.-Y. Li, Y.-C. Zhao, Innovative combination of electrolysis and Fe (II)-activated persulfate oxidation for improving the dewaterability of waste activated sludge, Bioresour. Technol. 136 (2013) 654–663.
[36] Y. Li, X. Yuan, Z. Wu, H. Wang, Z. Xiao, Y. Wu, X. Chen, G. Zeng, Enhancing the sludge dewaterability by electrolysis/electrocoagulation combined with zero-valent iron activated persulfate process, Chem. Eng. J. 303 (2016) 636–645.
[37] J.E. Silveira, J.A. Zazo, G. Pliego, J.A. Casas, Landfill leachate treatment by sequential combination of activated persulfate and Fenton oxidation, Waste Manag. 81 (2018) 220–225.
[38] L.-J. Song, N.-W. Zhu, H.-P. Yuan, Y. Hong, J. Ding, Enhancement of waste activated sludge aerobic digestion by electrochemical pre-treatment, Water Res. 44 (2010) 4371–4378.
[39] K. Chen, H. Lei, Y. Li, H. Li, X. Zhang, C. Yao, Physical and chemical characteristics of waste activated sludge treated with electric field, Process Saf Environ 89 (2011) 327–333.
[40] H. Gharibi, M.H. Sowlat, A.H. Mahvi, M. Keshavarz, M.H. Safari, S. Lotfi, M.B. Abadi, A. Alijanzadeh, Performance evaluation of a bipolar electrolysis/electrocoagulation (EL/EC) reactor to enhance the sludge dewaterability, Chemosphere 90 (2013) 1487–1494.
[41] G. Erden, Disintegration of biological sludge by electro-oxidation process with different electrode couples, Waste Biomass Valorization (2019) 1–7.
[42] H. Masihi, G.B. Gholikandi, Employing Electrochemical-Fenton process for conditioning and dewatering of anaerobically digested sludge: a novel approach, Water Res. 144 (2018) 373–382.
[43] M.S. Kim, K.-M. Lee, H.-E. Kim, H.-J. Lee, C. Lee, C. Lee, Disintegration of waste activated sludge by thermally-activated persulfates for enhanced dewaterability, Environ. Sci. Technol. 50 (2016) 7106–7115.
[44] K. Xiao, Y. Chen, X. Jiang, Q. Yang, W.Y. Seow, W. Zhu, Y. Zhou, Variations in physical, chemical and biological properties in relation to sludge dewaterability under Fe (II)–Oxone conditioning, Water Res. 109 (2017) 13–23.
[45] B. Jin, J. Niu, J. Dai, N. Li, P. Zhou, J. Niu, J. Zhang, H. Tao, Z. Ma, Z. Zhang, New insights into the enhancement of biochemical degradation potential from waste activated sludge with low organic content by Potassium Monopersulfate treatment, Bioresour. Technol. 265 (2018) 8–16.
[46] X. Zhou, Q. Wang, G. Jiang, P. Liu, Z. Yuan, A novel conditioning process for enhancing dewaterability of waste activated sludge by combination of zero-valent iron and persulfate, Bioresour. Technol. 185 (2015) 416–420.
[47] O.H. Lowry, N.J. Rosebrough, A.L. Farr, R.J. Randall, Protein measurement with the Folin phenol reagent, J. Biol. Chem. 193 (1951) 265–275.
[48] M. Dubois, K.A. Gilles, J.K. Hamilton, P.T. Rebers, F. Smith, Colorimetric method for determination of sugars and related substances, Anal. Chem. 28 (1956) 350–356.
[49] A. Eaton, L. Clesceri, E. Rice, A. Greenberg, M. Franson, Standard Methods for the Examination of Water and Wastewater, 21st edn., American Public Health Association, American Waterworks Association, Water Environmental Federation, Federation, Washington DC, 2005, pp. 1–88.
[50] O.G. Apul, F.D. Sanin, Ultrasonic pretreatment and subsequent anaerobic digestion under different operational conditions, Bioresour. Technol. 101 (2010) 8984–8992.
[51] S. Hong, H. Zhang, C.M. Duttweiler, A.T. Lemley, Degradation of methyl tertiary-butyl ether (MTBE) by anodic Fenton treatment, J. Hazard. Mater. 144 (2007) 29–40.
[52] C. Cai, H. Zhang, X. Zhong, L. Hou, Ultrasound enhanced heterogeneous activation of peroxymonosulfate by a bimetallic Fe–Co/SBA-15 catalyst for the degradation of Orange II in water, J. Hazard. Mater. 283 (2015) 70–79.
[53] Y. Li, X. Yuan, D. Wang, H. Wang, Z. Wu, L. Jiang, D. Mo, G. Yang, R. Guan, G. Zeng, Recyclable zero-valent iron activating peroxymonosulfate synchronously combined with thermal treatment enhances sludge dewaterability by altering physicochemical and biological properties, Bioresour. Technol. 262 (2018) 294–301.
[54] M. Basuvaraj, J. Fein, S.N. Liss, Protein and polysaccharide content of tightly and loosely bound extracellular polymeric substances and the development of a granular activated sludge floc, Water Res. 82 (2015) 104–117.
[55] J. Liang, J. Huang, S. Zhang, X. Yang, S. Huang, L. Zheng, M. Ye, S. Sun, A highly efficient conditioning process to improve sludge dewaterability by combining calcium hypochlorite oxidation, ferric coagulant re-flocculation, and walnut shell skeleton construction, Chem. Eng. J. 361 (2019) 1462–1478.
[56] K.-M. Lee, M.S. Kim, C. Lee, Oxidative treatment of waste activated sludge by different activated persulfate systems for enhancing sludge dewaterability, Sustain. Environ. Res. 26 (2016) 177–183.
[57] B. Fr, T. Griebe, P. Nielsen, Enzymatic activity in the activated-sludge floc matrix, Appl. Microbiol. Biotechnol. 43 (1995) 755–761.
[58] B. Liao, D. Allen, I. Droppo, G. Leppard, S. Liss, Surface properties of sludge and their role in bioflocculation and settleability, Water Res. 35 (2001) 339–350.
[59] K. Xiao, J. Deng, L. Zeng, T. Guo, Y. Gong, B. Yang, X. Zhao, H. Duan, Enhancement of municipal sludge dewaterability by electrochemical pretreatment, J. Environ. Sci. 75 (2019) 98–104.
[60] G.-H. Yu, P.-J. He, L.-M. Shao, P.-P. He, Stratification structure of sludge flocs with implications to dewaterability, Environ. Sci. Technol. 42 (2008) 7944–7949.
[61] S. Liming, H. Peipei, Y. Guanghui, H. Pinjing, Effect of proteins, polysaccharides, and particle sizes on sludge dewaterability, J. Environ. Sci. 21 (2009) 83–88.