



Corona discharge plasma-based degradation of simulated residual linear alkylbenzene sulphonate and dodecyl benzene sulfonate surfactants

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Abstract

Synthetic surfactants are used in a wide range of products ranging from household cleaning detergents to pesticide formulations. Due to their widespread use, residual surfactants are often released in large quantities into the environment, especially via wastewater and can act as potential toxicants. The present study explored the applicability of a non-thermal plasma, namely corona discharge plasma jet (CDPJ), for the degradation of residual surfactants so as to minimize their harmful effects to aquatic life. The plasma was generated using 20 kV DC power supply, with different input currents (1.00, 1.25 and 1.50 A) and at various electrode-to-sample distances (20, 25 and 30 mm). For degradation treatments, simulated residual surfactants (sodium dodecylbenzene sulfonate [DBS] and sodium linear alkylbenzene sulfonate [LAS]) and DBS-containing dishwashing detergents dispersed on slide glasses were exposed to CDPJ for predetermined periods of time (0–120 min). Results indicated that under optimal treatment conditions of 1.5 A current and 20 mm electrode-to-sample distance, the tested surfactants and surfactants in detergents were maximally degraded to about 57% following the plasma treatment for 120 min. Modeling of degradation kinetics indicated that Weibull distribution was the best-fit model, and decimal degradation times (δ) were calculated for different treatment conditions. The pure surfactants were degraded to a greater extent than surfactants in detergents.

Keywords Cold plasma · Sodium dodecylbenzene sulfonate · Sodium linear alkylbenzene sulfonate · Detergent · Kinetic modeling

Introduction

Surfactants or surface-active agents find wide applications as detergents, wetting agents, emulsifiers, foaming agents, dispersants, etc. They are predominant components in household detergents, such as laundry detergents, personal toiletries, and home cleaning supplies (Yuan et al. 2014). As a result of their widespread use, large volumes of wastewater that contain high levels of residual surfactants are often discharged into the environment. Such unchecked discharges are known to result in pollution of water bodies, harm to

aquatic life, and, in turn, endanger human health (Akkan 2017). On the other hand, detergents consist of surfactants together with subsidiary components including fillers, builders, boosters, and auxiliary compounds. Surfactants and builders (e.g., tripolyphosphate) in detergents are considered as compounds of environmental concern (Uc-Peraza and Delgado-Blas 2015). Environmental contamination from surfactants followed the shift from the use of soap-based detergents to synthetic surfactants (Scott and Jones 2000). Synthetic surfactants and their degradation products possess potential health and environmental effects (Bandala et al. 2008).

Toxic effects of surfactants on the environment are evident and have been well characterized, including inhibition of enzyme activity (e.g., algae nitrogenase and microbial dehydrogenase) and remobilization of organic pollutants (Hrenovic and Ivankovic 2007). The environmental persistence of surfactants is well known (Ikehata and El-Din 2004). Due to their recalcitrant nature, the degradation of

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these molecules is difficult (Brisset et al. 2016). Advanced oxidation processes (AOPs) are being increasingly considered for their removal from usual effluents (Aonyas et al. 2016). The efficiency of ozonation and other AOPs using various combinations of ozone, ultraviolet (UV) light irradiation, hydrogen peroxide, and iron salts in degrading recalcitrant surfactants, including alkylphenol ethoxylates, linear alkylbenzene sulfonates, and quaternary ammonium surfactants, has been reviewed by Ikehata and El-Din (2004). Lin et al. (1999) reported the Fenton oxidation of surfactant [alkylbenzene sulfonate (ABS) and linear alkylbenzene sulfonate (LAS)] wastewater. Photo-Fenton process was successfully applied for the degradation of anionic surfactants, namely sodium dodecyl sulfate (SDS) and dodecylbenzenesulfonate (DBS) (Amat et al. 2004). In another study, the use of solar radiation has been shown to improve the degradation efficiency of Fenton and cobalt/peroxymonosulfate (Co/PMS) system in the degradation of SDS in wastewater (Bandala et al. 2008).

In recent times, AOPs based on non-thermal plasma (NTP) have gained greater prominence (Aonyas et al. 2016; Attri et al. 2016). This is mainly due to the fact that NTP can generate a wide range of reactive chemical species and they are known to exhibit high oxidation potentials. Such reactive species include, but not limited to, reactive oxygen species (ROS) (e.g., $\text{OH}^\cdot$, $^1\text{O}_2$, $\text{O}_2^\cdot$, $\text{HO}_2^\cdot$) and reactive nitrogen species (RNS) (e.g., NO_3^- , NO_2^- , ONOO^- , NO) (Attri et al. 2016). In a previous study, successful degradation of dyes, namely Congo red, methyl orange and methylene blue, following treatments with two different type atmospheric pressure plasma jets (APPJs) [a direct (D-APPJ) and an indirect (ID-APPJ)], has been reported (Attri et al. 2016). The potential of a hydro-non-thermal-plasma AOP system for efficient and cost-effective destruction of organic contaminants, namely trichloroethylene, 1,4-dioxane and N-nitrosodimethylamine, has been shown (Even-Ezra et al. 2009). In another study, a gliding arc plasma has been shown to be effective in degrading (~ 90% degradation in 500 min plasma treatment) sodium lauryl sulfate (NaLS) in a circulating reactor (Brisset et al. 2016).

Dodecylbenzene sulfonate-sodium salt (DBS) is an anionic surfactant, and it is the predominant constituent of linear alkylbenzene sulfonate-sodium salt (LAS). LAS is a widely used active surfactant in cleaners and detergents worldwide (de Almeida et al. 1994). Under anaerobic conditions, the biological degradation of LAS has been shown to be incomplete and slow (Bharadwaj and Ahluwalia 1996). Therefore, in the present study, the effectiveness of corona discharge plasma jet (CDPJ) was tested for the oxidative degradation of residual concentrations of DBS and LAS surfactants. In addition, the degradation of DBS as a component of dishwashing detergents by CDPJ was studied. This

study was conducted from September 2017 to May 2018 at Gachon University, Seongnam, Korea.

Materials and methods

Chemicals and reagents

DBS was purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). LAS was purchased from Alfa Aesar (Ward Hill, MA, USA). Dishwashing detergents, namely Product J (contained 9.11% w/w DBS surfactant), Product S (contained 9.76% w/w DBS) and Product P (contained 11.48% w/w DBS), were purchased from a local supermarket. The rest of the chemicals employed were of analytical grade.

CDPJ generation

CDPJ used for the degradation of surfactants was generated as described previously (Kim et al. 2015). Briefly, the plasma generating electrodes were powered by a high-voltage generator (20 kV DC output voltage and 58 kHz frequency) (Fig. 1). CDPJ generated at input currents of 1.00, 1.25 and 1.50 A was used in the experimentation. For plasma jet creation, a centrifugal air blower (rotational speed: 3312 rpm) was used, and about 2.5 m/s air velocity was noted at the tip of the electrodes. During CDPJ treatment, the distance between the electrodes and the sample stand was maintained at three different levels (20, 25 and 30 mm).

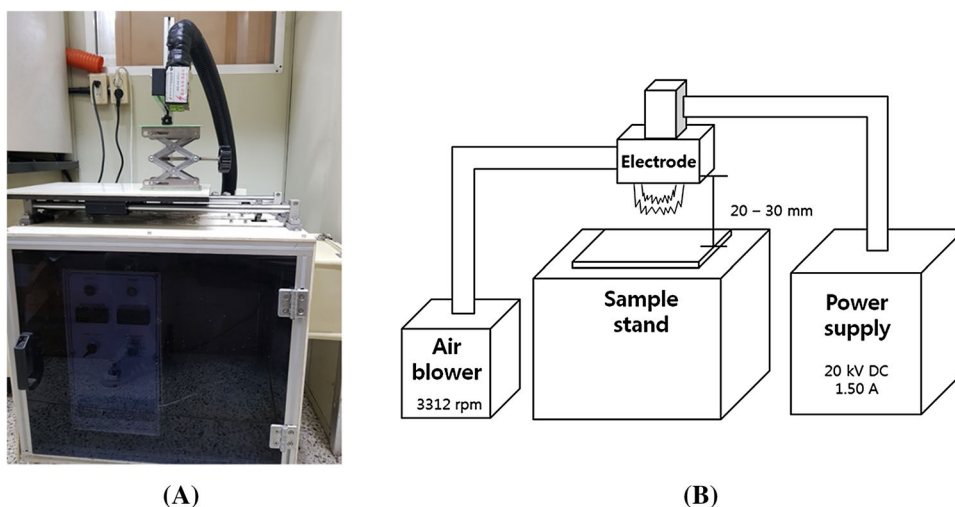
Degradation of simulated residual surfactants by CDPJ

Aqueous test solutions with surfactants (DBS and LAS, 3% w/w) and detergents (Product J, Product S and Product P, 10% w/w) were prepared using distilled water in order to simulate residual surfactant concentrations. Droplets of the samples were placed onto 76 × 26 mm glass slides (10 μL on each slide), spread and air-dried in a hood for 1 h. Subsequently, the slides were treated singly using CDPJ generated with different plasma currents (1.00, 1.25 and 1.50 A) and at different electrode-to-sample distances (20, 25 and 30 mm) for predetermined durations (0–120 min). Soon after treatment, remaining residual surfactants from the slides were retrieved using distilled water and quantified according to a spectrophotometric method using methylene blue (Ministry of Environment 2011).

Quantitation using the spectroscopic method

Into a separatory funnel, simulated residual surfactant or detergent solution (100 mL), methylene blue (MB) solution (5 mL) and phosphate buffer (10 mL, pH 10.0) were taken,

Fig. 1 Corona discharge plasma jet apparatus: **a** photograph of the apparatus; **b** schematic diagram of the apparatus



and further 100% chloroform (15 mL) was added to it. The entire mixture was vigorously shaken for 1 min and allowed to separate into two distinct layers. Later, lower layer was aspirated and transferred into a 2nd separatory funnel. About 15 mL of 100% chloroform was again added to the 1st funnel and repeated the steps to collect lower layer into the 2nd funnel. Thereafter, acidic MB solution (5 mL) and deionized water (100 mL) were added into the 2nd funnel collection, mixed well, and collected the lower layer in a volumetric flask (50 mL) via filtration through a glass microfiber filter. Into the remaining content in the 2nd funnel, 100% chloroform (5 mL) was added, shaken and collected the lower layer into the volumetric flask through filtration. This step was repeated once more. Lastly, the collected content of the volumetric flask was used for the quantification of simulated residual surfactant or surfactant in detergent using a spectrophotometer at 652 nm.

Degradation amount and modeling of degradation

The levels of surfactants degradation following CDPJ treatment were calculated, as shown in a previous study (Lee et al. 2019). We initially used log-linear model (Bigelow and Esty 1920) for kinetic modeling of CDPJ-induced degradation of the surfactants or surfactant in the detergents. Subsequently, the suitability of other models, namely log-linear tail (Geeraerd et al. 2000) and Weibull (Mafart et al. 2002), was tested and compared with the log-linear model. The equations for these kinetic models are substantially the same as those described in our previous study (Lee et al. 2019).

Statistical analysis

Results are shown as mean $\pm$ standard deviation (SD). Each treatment was replicated three times. A statistical software package, namely SAS (version 9.2, SAS Institute Inc., Cary,

NC, USA), was used for statistical analysis of data. The variance ($p < 0.05$) of the data was analyzed by one-way analysis of variance (ANOVA), followed by Duncan's multiple range test at $\alpha = 0.05$.

Results and discussion

Effect of electrode-to-sample distance and current on degradation

The electrode-to-sample distance influenced the degradation of the pure surfactants or the surfactant in the detergents on glass slides. An increase in the distance decreased the efficiency of degradation. At all tested electrode-to-sample distances (20, 25 and 30 mm), an increase in input current (1.00, 1.25 and 1.50 A) increased the efficiency of degradation for all tested surfactants or surfactant in detergents. In the case of DBS surfactant, a drastic reduction of initial concentration was observed upon CDPJ (generated using current of 1.50 A) treatment within 30 min, at all tested electrode-to-sample distances (Fig. 2). Thereafter, the rate of degradation was relatively slowed; $\geq 55\%$ degradation was noted within 120 min of CDPJ treatment at 20 mm electrode-to-sample distance. At 25 mm electrode-to-sample distance, the levels of remaining DBS concentration on glass slides following CDPJ treatment (for 120 min) at 1.0, 1.25 and 1.5 A were 54.8, 49.3 and 46.7% (of initial concentration), respectively. At 30-mm gap, remaining DBS levels after 120 min treatment were 64.8, 59.5 and 52.4% using CDPJ produced at 1.0, 1.25 and 1.5 A current, respectively.

Similar degradation patterns were observed in the case of LAS surfactant upon CDPJ exposure. The levels of remaining LAS concentration following CDPJ treatment (generated at 1.5 A current and treatment time of 120 min) at electrode-to-sample distances of 20, 25 and 30 mm were 42.7%, 49.5%



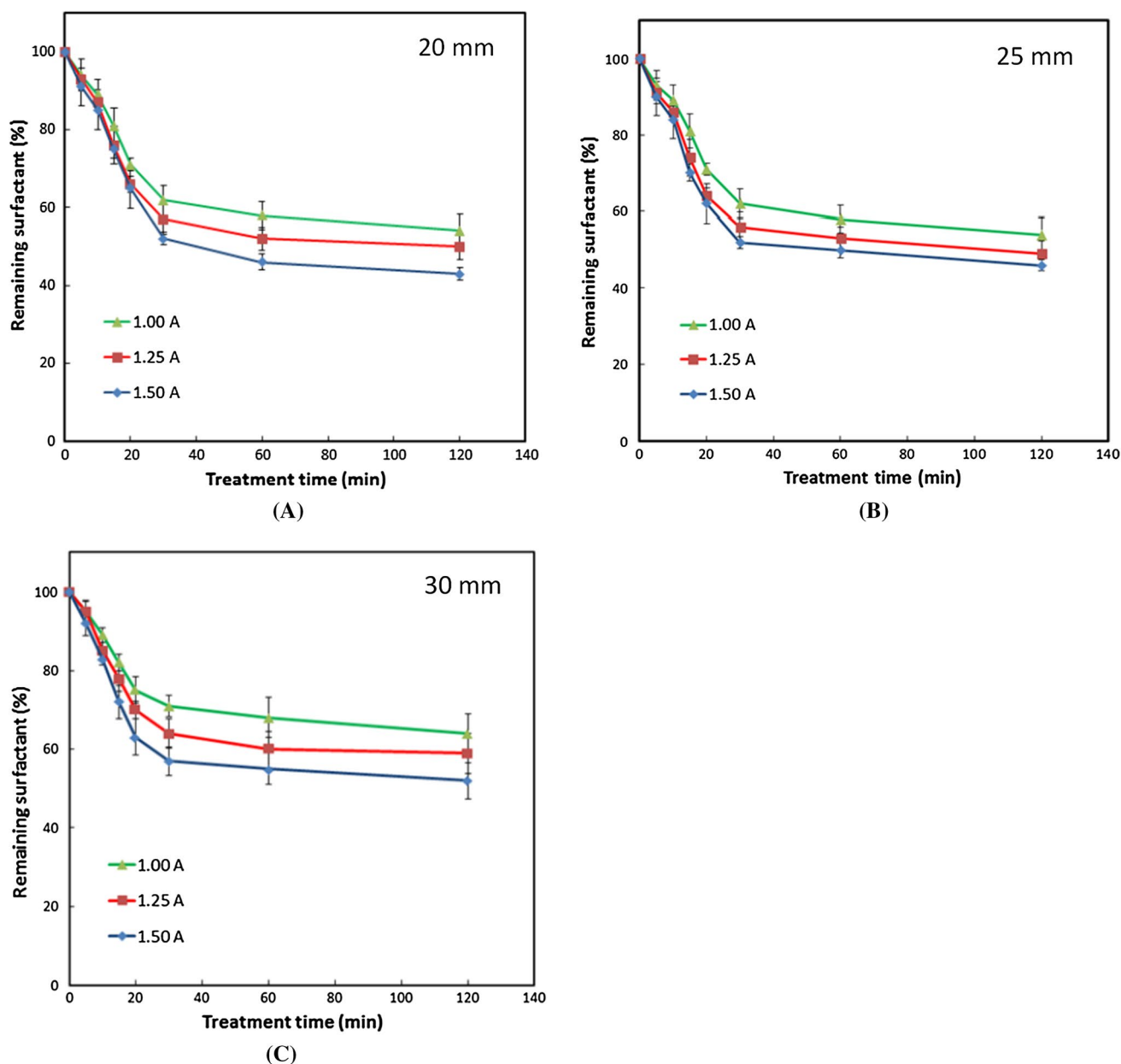


Fig. 2 Degradation patterns of DBS surfactant following CDPJ treatment at sample-to-electrode distances of 20 mm (a), 25 mm (b) and 30 mm (c)

and 50.8%, respectively. At other tested current levels, the efficiency of LAS degradation was relatively low, as shown in Fig. 3. On the other hand, in the case of Product J, Product S and Product P detergents, % remaining surfactant in detergents following CDPJ treatment (generated at 1.5 A current and treatment time of 120 min) at electrode-to-sample distance of 20 mm was 50.4, 50.1 and 51.4, respectively (Fig. 4).

These results indicated that the initial concentrations of DBS and LAS surfactants on glass slides can be degraded maximally up to 57% using CDPJ generated with 1.5 A

current, at 20 mm electrode-to-sample distance and a treatment time of 120 min. Under these conditions, the surfactant in tested detergents was degraded by approx. 50%.

These degradation trends could be due to the fact that the increasing current results in a higher power density (W/mm^3) throughout the plasma generation region thus increasing generation and density of the active, energetic plasma species that break-up surfactant molecules. Extending the distance between the surfactants and the plasma electrode means that less active species generated by the plasma will survive without recombination



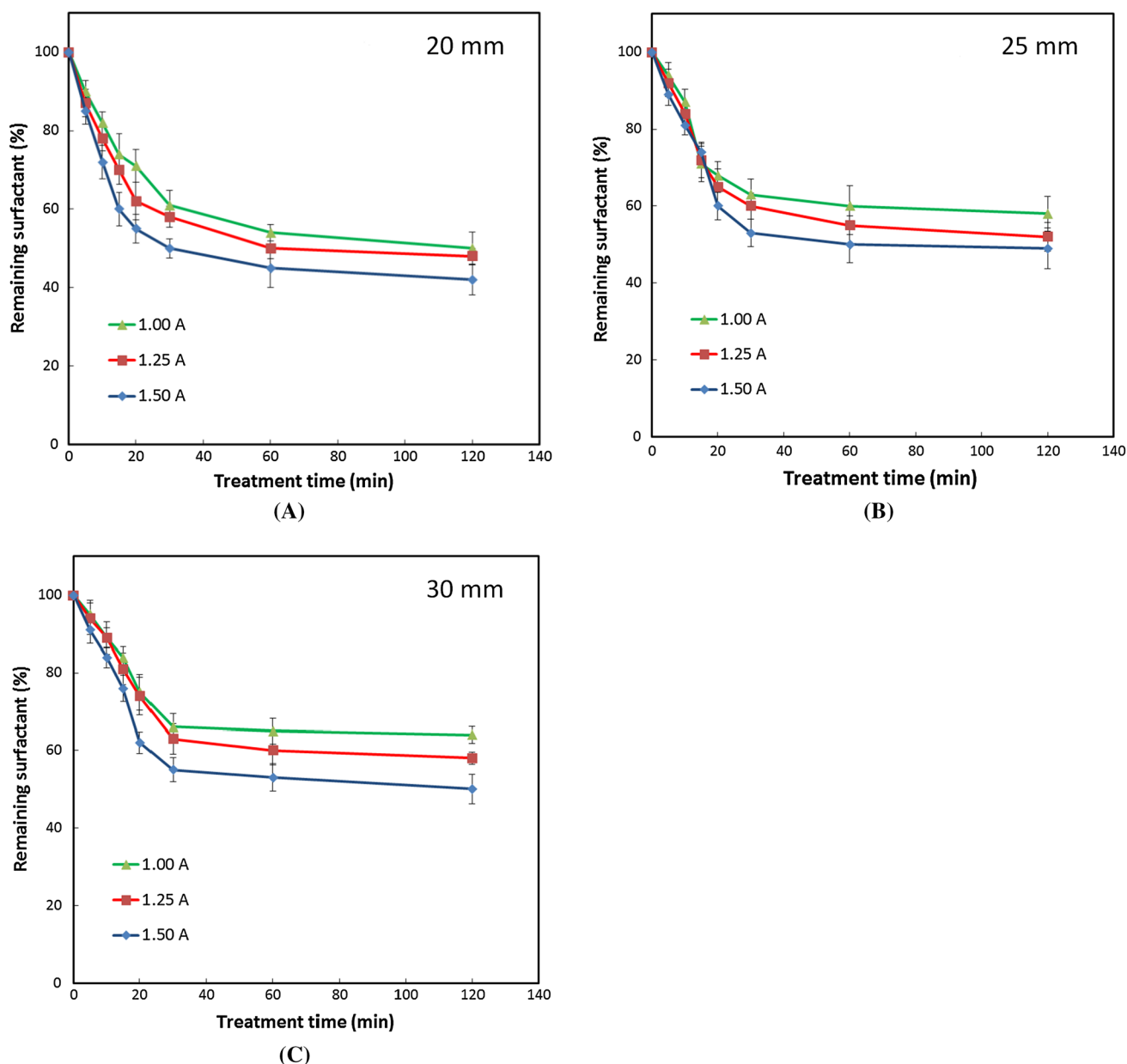


Fig. 3 Degradation patterns of LAS surfactant following CDPJ treatment at sample-to-electrode distances of 20 mm (a), 25 mm (b) and 30 mm (c)

and, thus, quenching of their chemical energy to reach surfactant molecules. Thus, the greater the distance, the lesser the effect.

In a previous study, dielectric barrier discharge (DBD) with falling liquid film has been shown to be effective for the degradation of two anionic surfactants (sodium lauryl sulfate—SDS and sodium dodecylbenzenesulfonate—SDBS). Results of that study showed that both surfactants (initial concentration of 100 mg L^{-1}) exhibited similar degradation trends and degradation efficiencies were nearly 90% (Aonyas et al. 2016).

The degradation with time seems to saturate in the present study. Such degradation saturation could be due to the inability of plasma reactive species to reach inner layers (of surfactant coat on slides). It seems large-sized plasma-surfactant reaction by-products on top monolayers act as shield preventing the active chemical species further penetration. Thus, by-product desorption techniques could eliminate the saturation limitation.



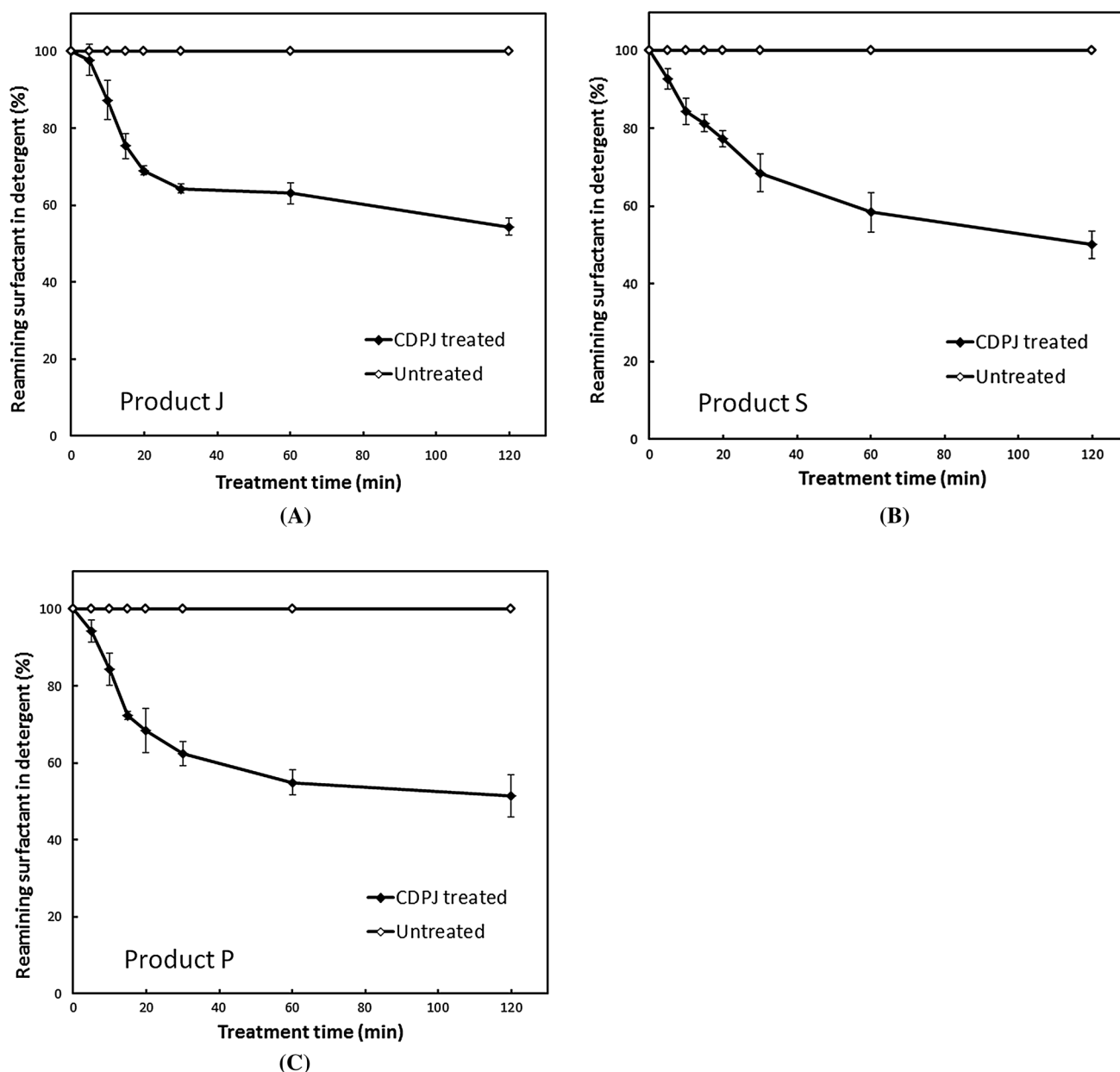


Fig. 4 Degradation patterns of DBS surfactant in detergents, Product J (a), Product S (b) and Product P (c), following CDPJ (generated at 1.5 A current) treatment at a sample-to-electrode distance of 20 mm

Kinetics of degradation

The suitability of chosen models, including log linear, log-linear tail and Weibull, to explain CDPJ-induced surfactant (DBS and LAS) degradation was tested. Based on the obtained data, Weibull model was found to be the best-fit model. The Weibull model fits the degradation data well as evidenced from the values of root mean squared error (RMSE), sum of squared errors (SSE) and coefficient of determination (R^2). A relatively high R^2 value (close to 1) and low RMSE and SSE values for Weibull model indicated

Table 1 Sum of squared errors (SSE), root mean squared error (RMSE) and coefficient of determination (R^2) obtained for tested models

Model type	SSE	RMSE	R^2 value
Log linear	0.0246 ± 0.0072	0.1569 ± 0.0848	0.7810 ± 0.0447
Log linear tail	0.0075 ± 0.0033	0.0842 ± 0.0194	0.9194 ± 0.0287
Weibull	0.0010 ± 0.0006	0.0311 ± 0.0084	0.9876 ± 0.0083



Table 2 δ -values (first decimal reduction time) obtained for DBS and LAS degradation using CDPJ at different electrode-to-sample gaps

Electrode-to-sample distance (mm)	Current (A)	δ (min)	
		DBS	LAS
20	1.00	488.12 $\pm$ 114.45 ^b	512.38 $\pm$ 245.42 ^b
	1.25	411.28 $\pm$ 187.42 ^c	475.45 $\pm$ 154.21 ^c
	1.50	221.12 $\pm$ 124.45 ^d	248.45 $\pm$ 114.54 ^d
25	1.00	687.22 $\pm$ 182.24 ^a	755.33 $\pm$ 184.24 ^{ab}
	1.25	554.55 $\pm$ 101.44 ^{ab}	538.87 $\pm$ 132.12 ^b
	1.50	397.45 $\pm$ 138.45 ^c	375.56 $\pm$ 145.87 ^c
30	1.00	734.55 $\pm$ 172.87 ^a	887.76 $\pm$ 233.75 ^a
	1.25	612.77 $\pm$ 148.45 ^{ab}	642.87 $\pm$ 178.45 ^b
	1.50	487.95 $\pm$ 108.78 ^c	438.27 $\pm$ 127.33 ^c

Values are given as mean $\pm$ SD ($n=3$). Distinct letter within the same column indicate significant differences ($p < 0.05$)

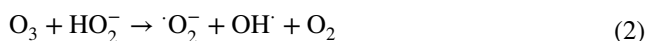
that the model is the best-fitting model compared with others (Table 1). The Weibull distribution can describe log-linear and non-log-linear kinetics. In a previous study, similar patterns of degradation were noted for NaLS degradation by a gliding arc discharge (Brisset et al. 2016). They found that initial stages of degradation were governed by a pseudo-zero-order rate law and subsequent stages were governed by a pseudo-first-order decay.

The Weibull model was also used to explain surfactant (DBS and LAS) degradation at different process variables. As can be seen from Table 2, relatively low δ -values (time to the first decimal reduction) were observed for both DBS and LAS degradation using CDPJ generated at 1.5 A current and 20 mm electrode-to-sample distance.

Possible degradation mechanism

Corona discharges have been shown to produce ozone, ROS, hydrogen peroxide, nitrogen, hydrogen and OH radicals, as well as other chemically active species (Timoshkin et al. 2012). Generally, ozone reacts swiftly with aqueous organic contaminants, especially those having a high electron density (i.e., strong nucleophiles) as well as hydroxyl or amine groups containing aliphatic and aromatic compounds (Aonyas 2016). Hydroxide ions initiate ozone decay, which leads to a series of reactions, resulting in generation of nonselective and fast-acting OH radicals. These radicals interact with target molecule at high electron density position.

With H_2O_2 presence in plasma, ozone can react with HO_2^- giving OH^- (Aonyas 2016).



RNS include nitric oxide, nitrous acid and peroxy-nitrous acid, their further oxidation leads to toxic NO_2^- and NO_3^- species formation. NO and NO_2 formed in plasma

phase can dissolve in water and interact with other plasma-generated active species such as O_3 , H_2O_2 and hydroperoxyl radical, resulting in the formation of other RNS such as HNO_2 (nitrous acid) and peroxy-nitrous acid (HNO_3) (Aonyas 2016).

Conclusion

Conditions for the oxidative degradation of residual levels of DBS and LAS as well as DBS in detergents by CDPJ were optimized. Under the optimal degradation conditions of 1.5 A current and 20 mm electrode-to-sample distance, the initial concentrations of DBS and LAS on glass slides were decreased by up to 57% in 120 min. Under the same treatment conditions, initial levels of DBS in tested detergents were degraded by up to 50%. The Weibull model was found to be best-fit model compared with others to explain kinetics of degradation of the surfactants (both in pure form and in detergent formulation) by the plasma.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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