

Nanoplastics removal from spiked laundry wastewater using electro-peroxidation process

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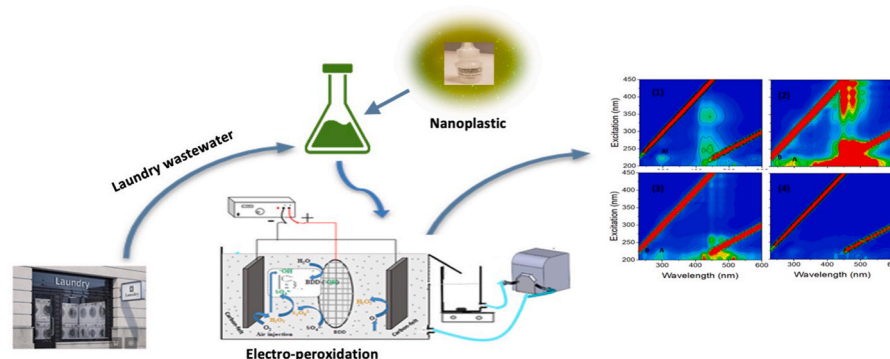
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HIGHLIGHTS

- Degradation of NPs in LWW using electro-peroxidation process is investigated.
- Chloride ion in commercial LWW could contribute to faster degradation of NPs.
- A parametric analysis of the process was performed using RSM models.
- Complete removal of NPs could be obtained as fast as 40 min.
- Humic acid-like compounds could be oxidized after 20 min of treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Microplastics and nanoplastics (NPs) in laundry wastewater (LWW) are major sources of plastic particles in wastewater treatment plants. Unlike microplastics, almost no information exists in the literature on the degradation of NPs in LWW. In this work, the degradation of NPs in commercial LWW by the electro-peroxidation process is investigated. The obtained results demonstrated that already existing ions in LWW such as Cl^- contribute to faster degradation of NPs and a complete removal could be obtained as fast as 40 min. In addition, three-dimensional excitation and emission matrix fluorescence analysis was performed, which revealed humic acid-like, aromatic proteins-like, and fulvic acid-like compounds could be oxidized after 20, 40, and 60 min of treatment respectively. The effects of operating parameters on the process performance were then examined by response surface methodology (RSM) models. The results showed that initial TOC concentration was the most important parameter influencing negatively the percentage of NP degradation. Afterward, optimization of the process revealed that the energy consumption could be minimized at 31.2 mA/cm^2 , 0.025 mol/L $[\text{Na}_2\text{SO}_4]$, and 52 min treatment time for 52.2 mg/L initial TOC. Finally, analysis of treated LWW showed no toxicity on *Daphnia magna*. This study showed that the electro-peroxidation process can completely degrade NPs in LWW without any remaining toxic compounds.

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1. Introduction

Over the last ten years, the microplastics (MPs) and nanoplastics (NPs) pollution sourced from plastics debris fragmentation, personal care products, and synthetic fabrics in the aquatic environment as well as their interaction with other contaminants like heavy metals, industrial dyes, and organic pollutants has been an increasing concern. These emerging pollutants are introduced into the aquatic systems mainly via wastewater treatment plant effluents (Henry et al., 2019; Iyare et al., 2020) and MP fibers are the most common form of them (Sun et al., 2019). Previous studies reported synthetic textile washing particles sourced from laundry wastewater (LWW) as an important source of MP fiber in municipal wastewater treatment plants (Acharya et al., 2021; Tian et al., 2021). MPs/NPs alone or combined with other pollutants showed some harmful effects on the reproduction, growth, feeding, and development of aquatic organism biological systems (Avio et al., 2015; Trestrail et al., 2020). Toxicological studies of MPs' effects on human health revealed MPs would be detected even in the human placenta and blood samples (Leslie et al., 2022; Ragusa et al., 2021). These pollutants are suspected to affect mainly the human intestinal microbiome and cause pulmonary cytotoxicity *in vitro* (Dong et al., 2020; Smith et al., 2018). In real daily life, polystyrene (PS) is one of the most widely used plastics (over 23 million tons per year) (Lithner et al., 2011), making it one of the most significant constituents of NPs. Polystyrene is a thermoplastic material used in various applications, including clothing in the apparel and textile industry, particularly in 3D printing of textiles technology to obtain some unique characteristics like strength and flexibility of textiles (Chatterjee and Ghosh, 2020; Korger et al., 2020). In addition, polystyrene is one of the most often used polymers to study the toxicity of plastics (Wang et al., 2021). Concerning their harmful effects and the inability of conventional water treatment processes to efficiently remove MPs/NPs as reported in previous studies (Carr et al., 2016; Sun et al., 2019; Zhang et al., 2020; Ziajahromi et al., 2017), an effective treatment technology is strongly desired to remove these pollutants from their main sources in the aquatic environment, particularly laundry and textile effluents.

Filtration (Simon et al., 2018; Talvitie et al., 2017), flocculation-precipitation (Murray and Örmeci, 2020; Zhang et al., 2021), membrane filtration (Lares et al., 2018; Pizzichetti et al., 2021), and electrocoagulation (Perren et al., 2018; Shen et al., 2022) have been studied as alternative methods to remove MPs/NPs in aqueous matrix. These methods are based only on the transfer phase, and a second treatment is necessary to degrade or mineralize the transferred MPs/NPs in the solid phase. For the degradation of MPs/NPs, recent studies have focused on the investigation of advanced oxidation processes (AOPs) such as catalytic activation of peroxymonosulfate (Kang et al., 2019), electro-Fenton-like (Miao et al., 2020), and electro-peroxidation ($\text{EO-H}_2\text{O}_2$) (Kiendrebego et al., 2022). Although the previous studies using AOPs demonstrated a high efficiency of MPs/NPs degradation, most studies were carried out using synthetic effluents. So, there is a lack of knowledge dealing with MPs/NPs degradation in real effluents. In real effluents, the interaction effects of MPs/NPs with other compounds should be considered.

Among the AOPs, the electro-peroxidation process utilizes diverse ROSs (reactive oxygen species) to completely mineralize MPs/NPs in water. Sulfate radical ($\text{SO}_4^\bullet$, $E_0 = 3.1 \text{ V vs NHE}$) and hydroxyl radical ($^\bullet\text{OH}$, $E_0 = 2.8 \text{ V vs NHE}$) represent powerful oxidants to decompose a large spectrum of refractory organic contaminants in complex water matrices (Buxton et al., 1988; Ren et al., 2015). In this process, boron-doped diamond (BDD) can be used as an effective electrode to produce hydroxyl radicals from water discharge (Panizza and Cerisola, 2005) and also generate peroxymonosulfate in an electrolyte medium containing sodium sulfate (Davis et al., 2014; Divyapriya and Nidheesh, 2021). Peroxymonosulfate has been widely applied in AOPs to produce $\text{SO}_4^{\bullet-}$ and $^\bullet\text{OH}$ radicals (Dos Santos et al., 2020; Hilles et al., 2016). Despite this, the electro-peroxidation process has some drawbacks

including limitations in the treatment of industrial effluent as well as its high operating cost due to extensive electrical energy consumption. To the best knowledge of the authors, the application of electro-peroxidation in the degradation of NPs in industrial laundry effluents has not been investigated.

The present work studies the degradation of NPs in commercial LWW using the electro-peroxidation process. In this regard, commercial LWW samples with a defined concentration of NPs were prepared and treated in an electrochemical reactor. The rates of NP removal and total organic carbon (TOC) removal were analyzed during the treatment process to evaluate the process efficacy as well as the interaction effect of NPs and organic compounds in LWW. In addition, three-dimensional excitation and emission matrix fluorescence (3D EEM) analysis was performed to explore NPs destruction mechanisms. Afterward, response surface methodology (RSM) models were developed to predict the rate of NPs removal, TOC removal, and energy consumption as a function of current density, electrolyte concentration, electrolysis time, and initial TOC concentration. In addition to the parametric study of the process, the developed model was used to optimize the value of operating parameters and minimize the operating cost. Finally, the toxicity of samples before and after treatment was analyzed by evaluating the *Daphnia magna* populations.

2. Materials and methods

2.1. Chemicals

Polystyrene NP suspension (CAS # FSSP9713546, EA BLU FL PS 0.15 μM 1% solid by weight) was purchased from Thermo Fisher Scientific. Reagent-grade anhydrous sodium sulfate (purity >98%) was purchased from Sigma-Aldrich and used as an electrolyte.

2.2. Laundry wastewater sampling and characteristics

LWW was sampled in March, April, and June from an automated commercial laundry facility in Québec City and coded as S1, S2, and S3, respectively. The samples were collected at the outlet of washing machines and stored in polypropylene bottles at 4 °C. The effluents were pre-filtrated with a glass microfiber filter (pore size 1.6 μm) to eliminate suspended solids. The composition of raw and filtered LWW is shown in Table 1. As can be seen in this table, the filtration only changed turbidity, COD, and TSS.

2.3. LWW NP-spiking

To analyze the performance of the electro-peroxidation process in the degradation of NPs in laundry real effluents containing organic matter, filtered LWW samples were enriched with NPs to obtain 1 L of LWW sample with a final concentration of 10 mg/L. This has been performed by the addition of a supporting electrolyte as well as synthetic water to filtered LWW to obtain Na_2SO_4 concentrations as presented in Table 1. The LWW NP-spiked samples were coded as NP-S1, NP-S2, and NP-S3. For comparison purposes, synthetic water (NP-SW) was prepared by adding NPs to deionized water in the absence of LWW. NP-SW is the used sample in our previous work (Kiendrebego et al., 2022) and allowed to compare NP degradation in industrial wastewater with pure water matrices. Before electro-peroxidation treatment, the mixtures were mixed for 20 min to be completely homogenized.

2.4. Electrolytic reactor setup

Experiments were carried out in batch mode by recirculating the effluent in an undivided single parallelepipedic reactor made of Plexiglas with a dimension of $14.5 \times 6.4 \times 17.7 \text{ cm}$ and a useful volume of 800 mL. A volume of 200 mL was recirculated in another tank (500 mL of capacity) made of Plexiglas. The degradation of NPs was conducted

Table 1
Characteristics of raw and pre-treated LWW samples.

Parameters	S1		S2		S3	
	Raw eff.	Filtrate	Raw eff.	Filtrate	Raw eff.	Filtrate
Turbidity (NTU)	25.7	3.51	23.6	3.26	24.7	3.30
COD (mg/L)	–	244 ± 12	–	389.5 ± 49	–	241 ± 38
TSS (mg/L)	45 ± 10	1.3 ± 0.5	50.0 ± 7.2	0.7 ± 0.2	20 ± 4.5	2.3 ± 0.7
pH	9.97 ± 0.30		10.50 ± 0.38		9.10 ± 0.50	
Conductivity (µS/cm)	849 ± 39		336 ± 31		289 ± 20	
NPEOs (µg/L)	570 ± 150		425 ± 100		237 ± 89	
SO ₄ ^{2−} (mg/L)	18.50 ± 0.14		15.00 ± 1.55		16.80 ± 0.21	
Cl [−] (mg/L)	145.00 ± 1.41		160.00 ± 2.90		153.00 ± 2.121	
Na (mg/L)	145.00 ± 0.00		110.00 ± 0.75		127.50 ± 0.00	
Al (mg/L)	0.06 ± 0.01		0.08 ± 0.01		0.07 ± 0.03	
Ca (mg/L)	17.15 ± 0.21		19.10 ± 1.27		18.20 ± 0.25	
Mg (mg/L)	2.22 ± 0.08		2.87 ± 0.42		2.58 ± 0.33	
K (mg/L)	1.66 ± 0.03		3.51 ± 1.29		2.6 ± 0.01	
S (mg/L)	7.37 ± 0.09		6.40 ± 0.73		6.92 ± 0.04	
Si (mg/L)	6.65 ± 0.02		7.20 ± 0.38		6.93 ± 0.09	
B (mg/L)	0.01 ± 0.00		0.01 ± 0.00		0.01 ± 0.01	
Ba (mg/L)	0.05 ± 0.02		0.03 ± 0.02		0.05 ± 0.02	
Sr (mg/L)	0.08 ± 0.00		0.1 ± 0.01		0.09 ± 0.00	
Zn (mg/L)	0.05 ± 0.00		0.350 ± 0.21		0.20 ± 0.02	
Fe (mg/L)	0.07 ± 0.01		0.05 ± 0.03		0.02 ± 0.02	

using the EO process with in-situ H₂O₂ generation (EO-H₂O₂ process). The application of the EO-H₂O₂ process consisted in treating NPs with an electrochemical reactor (CF-BDD-CF configuration) comprising one BDD electrode installed between two CF electrodes (CF represents carbon felt and BDD for boron-doped diamond). CF was used as a cathode electrode, whereas BDD was used as an anode electrode. The electrode set consisted of one anode and two cathodes with a distance between the electrodes of 10 mm. One niobium-covered BDD circular-mesh electrode with a diameter of 12 cm, a thickness of 0.1 cm, and a surface area of 113.1 cm² was used as the anode. In addition, two carbon-felt electrodes with an 11 cm (length) × 9 cm (width) rectangular shape and a thickness of 1 cm were employed as the cathodes. The agitation and homogenization of the solution were carried out using a PTFE-coated magnetic stirrer during electrolysis. The electro-peroxidation treatment of NP in the LWW was performed at room temperature. The solutions were continuously saturated with O₂ by bubbling compressed air at atmospheric pressure at a rate of about 0.9 L/min.

2.5. Experimental procedure

The first sets of electro-peroxidation experiments were conducted in three LWW NP-spiked samples containing different initial organic matter under the best conditions determined with synthetic water. Anodic current density and Na₂SO₄ concentration were 36 mA/cm² and 0.03 mol/L, respectively. The recirculation flow rate and treatment time were respectively fixed at 400 mL/min and 1 h. During these tests, the concentration of NPs was analyzed using UV–Vis spectrophotometry at 225 nm wavelength, as discussed in section 2.7.1. In addition, TOC and 3D-EEM analyses were performed to evaluate the performance of the process. A central composite design (CCD) was applied to define the optimal conditions and analyze the parameters of the electro-peroxidation process in treating laundry effluents doped with NPs, as explained in section 2.6.

2.6. Experimental design and modeling

For statistical and ANOVA analysis, Design-Expert software version 13 (Stat-Ease Inc., USA) was used to design the experiments and develop an RSM model. The experiments region investigated for LWW treatment

and the code values are shown in Table S1. Experiments were defined using a factorial design and central composite design (CCD) method. Current density (X₁), Na₂SO₄ concentration (X₂), electrolysis time (X₃), and initial TOC concentration (X₄) were defined as independent variables. Initial TOC was defined based on FD in two levels while other independent variables were defined based on CCD in five levels. The range of independent variables was selected based on previous pre-experiments. On the other hand, NP removal efficiency (Y_{NP}), TOC removal efficiency (Y_{TOC}), and energy consumption (Y_{Energy}) were considered dependent variables (responses). Tables 2 and Table S2 present the value of the independent variables along with the experimental values of responses. As seen, a total number of 32 experiments were defined which includes 16 factorial points (2^k, where k is the number of factors), 14 non-center points, and 2 replicated center points. Using the experimental values, a Response Surface Methodology (RSM) model was developed to model the responses as a function of independent parameters. In addition to parametric analysis, the developed RSM model was used to optimize the independent variables.

2.7. Analytical methods

2.7.1. NP quantification

The UV–Vis absorbance of NPs was determined at different concentrations by UV–Vis spectrophotometric measurements (UV0811M136). The UV–Vis absorption spectroscopy results of NPs as a function of NP concentrations in the range of 0–12 mg/L are presented in Fig. S1. The maximum absorption of NP was determined to be at 225 nm (Fig. S1a). Using the absorption values obtained at this wavelength, a calibration curve was plotted that shows the NP absorbance increases linearly by NP concentration with an R² = 0.9964 (Fig. S1b). This calibration curve was used to calculate residual NP concentration and define the NP removal efficiency with Eq. (1).

$$NP\ removal\ (\%) = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

where C_i and C_t represent the initial NP concentration and residual NP concentration after t minutes of electrolysis.

2.7.2. 3D EEM analysis

LWW samples were characterized using three-dimensional fluorescence excitation-emission matrices (3D EEM) with Cary Eclipse Fluorescence Spectrophotometer from Varian Inc. (USA). The method used for the NP-doped LWW fluorescence spectra collection was referred to as domestic wastewater Effluents Organic Matter (EfOM) characterization in full-scale MBR (Jacquin et al., 2017). Data were extracted following the division of the 3D fluorescence spectra representation into five different areas corresponding to different groups of fluorophores (Chen et al., 2003). The spectra were collected from 230 to 450 nm at 10 nm increments by varying the excitation from 200 to 450 nm at 5 nm intervals.

2.7.3. Total organic carbon analysis

TOC analysis was performed using TOC-L Shimadzu 1.05.00 analyzer to verify the effectiveness of the electro-peroxidation process. TOC was considered as the difference between total carbon and inorganic carbon.

2.8. Economic analysis

Economic analysis of electrochemical water treatment processes is one of the major aspects to take into consideration because of its high amount of energy consumption. Energy consumption was calculated using Eq. (2).

$$EC\ (kWh.m^{-3}) = \frac{U \times I \times t}{V} \times 10^3 \quad (2)$$

where U , I , t , and V represent average cell voltage (V), applied current intensity (A), duration of electrolysis (h), and volume of treated solution (m^3), respectively. It is worth noting that the energy consumption for pumping oxygen is negligible compared to the energy required for the EO process. It is a reason for which it has not been considered in this work.

2.9. Acute toxicity assessments

Toxicity tests were performed with *Daphnia magna* hatchling (<24 h old) from Bureau Veritas laboratory culture at Saint-Laurent, Quebec. Their culture medium was reconstituted water with the following characteristics: 180 mg $CaCO_3/L$ hardness, $\geq 80\%$ dissolved oxygen, pH of 7–8, 20.0 ± 2.0 °C temperature, and 16 h light – 8 h dark photoperiod). The organisms were fed once a day following MA. 500-D.mag. analytical method, *Daphnia magna* (<24 h old) was exposed to 48 h, to non-doped LWW as well as NPs-doped LWW before and after treatment. For this analysis, 0.00%, 6.25%, 12.50%, 25.00%, 50.00%, and 100.00% concentrations (v/v) were evaluated. Four replicates were performed for each concentration, with five hatchlings per test, placed in a bottle containing 10 mL of reconstituted water and LWW. Control tests were performed simultaneously to assure the accuracy of results. 37.5 ± 12.5 mL/min/L air flow was applied for 30 min before starting the experiments to maintain the dissolved oxygen content close to 100%. Additive effects of chemical, biological, and physical parameters of effluents were evaluated through pH, hardness, dissolved oxygen, temperature, and conductivity measurements before and after 48 h of exposure. The visual method was used to evaluate the criteria of toxicity consisting of immobility (antennae movement) and mortality (swimming).

3. Results and discussion

3.1. NPs degradation analysis

The performance of the electro-peroxidation process to degrade NPs in wastewater was assessed by analyzing the concentration of remaining NPs during the treatment process. To do so, the degradation of NPs was first analyzed using synthetic water (SW) samples containing NPs (NP-SW) and the results were compared with NP samples in LWW containing organic matter (NP-S1, NP-S2, and NP-S3). The samples of NP-S1, NP-S2 and NP-S3 initially contained 52.2 ± 2.8 mg/L, 29.4 ± 0.6 mg/L and 16.3 ± 1.2 mg/L of TOC, respectively. The results of this comparison are demonstrated in Fig. 1a. The tests were performed at a current density of 36 mA/cm^2 and $0.03 \text{ mol/L Na}_2\text{SO}_4$ was used as an electrolyte during 1 h of electrolysis. As shown in Fig. 1a, for all the samples a high rate of NPs removal is observed up to around 30 min. Almost complete removal of NPs was achieved after 40 and 50 min of treatment for NP-S3 and NP-S2, respectively. However, around $89.4 \pm 2.6\%$ and $90.6 \pm 2.8\%$ removal efficiencies were obtained after 60 min for NP-SW and NP-S1, respectively. In real LWW artificially contaminated by NP, the best performances of the electro-peroxidation process were recorded ($\sim 100\%$ of NP degradation) while treating samples having relatively low initial TOC concentrations (16–29 mg/L). However, when the initial concentration of TOC increased (52 mg/L of TOC), the percentage of NP degradation decreased to 90%. Indeed, competitive reactions took place between NP oxidation versus TOC oxidation when the initial TOC concentration was relatively high in LWW. The faster degradation of NPs in LWW could be attributed to the production of a higher amount of $\bullet\text{OH}$, H_2O_2 , $\text{S}_2\text{O}_8^{2-}$, HOCl , and ClO^- . These ROSs could be generated in the electrolysis environment due to the initial presence of ions such as SO_4^{2-} and Cl^- (Table 1) sourced from bleach and surfactants widely used for disinfecting clothes in laundries. The BDD anode could form additional oxidants such as HOCl and ClO^- mainly in the bulk solution by Cl^- oxidation following reactions (3–5) (Garcia-Segura et al., 2015).

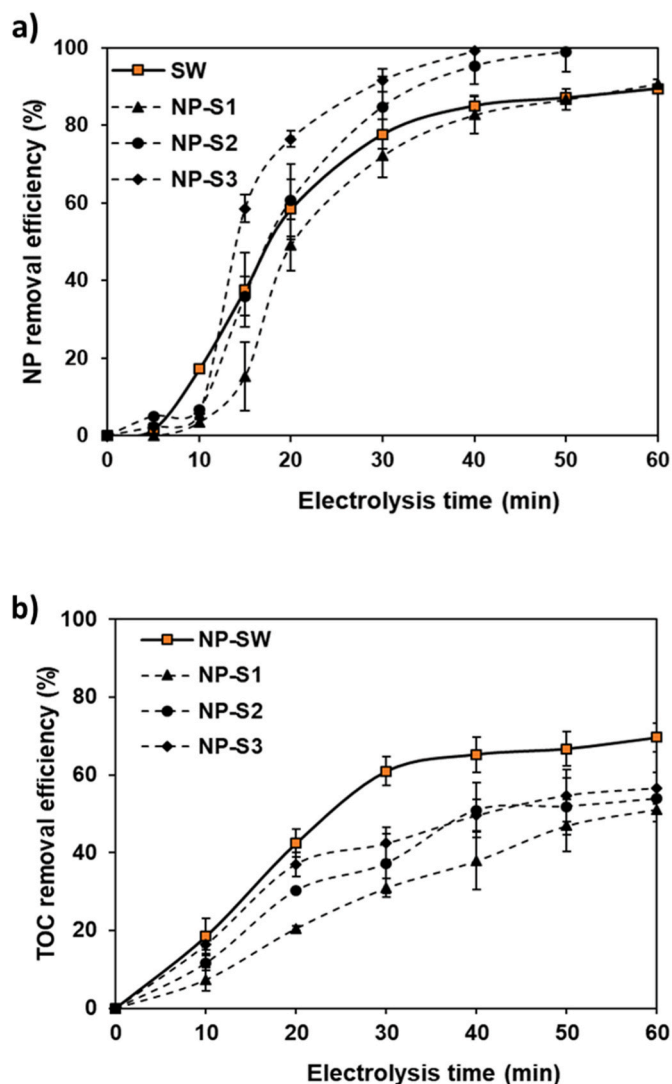


Fig. 1. a) Degradation rate of NPs and b) TOC removal efficiencies of synthetic water (NP-SW) as well as laundry wastewater samples (NP-S1, NP-S2, and NP-S3) at $[\text{Na}_2\text{SO}_4]$ of 0.03 mol/L and current density of 36 mA/cm^2 .

Likewise, in the presence of hydroxyl radicals, Cl^- ions are oxidized by $\bullet\text{OH}$ to ClO^- (Eq. (6)). The produced ClO^- can react with $\bullet\text{OH}$ in several steps to form different active chlorine species as presented in Eqs. (7)–(9).



By comparison, the NP degradation in SW (NP-SW samples) was mainly attributed to $\bullet\text{OH}$, H_2O_2 , $\text{S}_2\text{O}_8^{2-}$ generated during electrolysis. Analysis of the initial pH of the solution showed that the pH of LWW was around 10 (Table 1), while this was 5.70 ± 0.10 for the NP-SW sample.

After the electrolytic experiments, the pH dropped to 2.72 ± 0.2 after 20 min of electrolysis. This significant decrease even for synthetic water can be explained mainly by the reaction between sulfate radicals and electro-generated H_2O_2 in the solution (see Eqs. (11) and (12)) (Kiendrebego et al., 2022).



In our previous work (Kiendrebego et al., 2022), we investigated the produced ROSs ($^{\bullet}OH$, H_2O_2 , $S_2O_8^{2-}$) and their roles in the oxidation of NPs by EO and EO- H_2O_2 processes. It was found that in the EO process, NPs were mainly oxidized by two types of ROSs on the BDD surface: (i) $^{\bullet}OH$ from water discharge and (ii) $SO_4^{\bullet-}$ via $S_2O_8^{2-}$ reaction with $^{\bullet}OH$. In the EO- H_2O_2 process, NPs were additionally degraded by $^{\bullet}OH$ formed from H_2O_2 decomposition as well as $SO_4^{\bullet-}$ generated from direct or indirect reactions with H_2O_2 (Eq. (10)). Equations (11) and (12) show that protons (H^+) are released in water and induce a decrease of pH.

3.2. Total organic carbon analysis

TOC analysis was performed to evaluate the interaction effect of NP and organic matter initially present in the LWW. The initial TOC concentrations of NP-SW, NP-S1, NP-S2, and NP-S3 were 9.2 ± 0.7 , 52.2 ± 2.8 , 29.4 ± 0.6 , and 16.3 ± 1.2 mg/L, respectively. The final residual TOC concentrations after 60 min of electrolysis were 2.8, 29.2, 15.0, and 7.6 mg/L on average for NP-SW, NP-S1, NP-S2, and NP-S3, respectively. The variation of TOC during the electrolytic experiments for these four samples is shown in Fig. 1b. As seen, TOC removal efficiency for NP-SW reached a higher value in comparison to LWW samples. The TOC removal efficiencies were $69.6 \pm 0.5\%$ for NP-SW versus $51.1 \pm 3.3\%$, $53.8 \pm 2.3\%$, and $56.6 \pm 3.7\%$ for NP-S1, NP-S2, and NP-S3, respectively. The difference between the degradation kinetic of TOC removal efficiency of LWW samples would be attributed to various factors including the difference in initial TOC. Around 87% of TOC removal was reported in the previous works (Khosravanipour Mostafazadeh et al., 2019) using electrolytic treatment of LWW concentrate containing 2 times more COD than the filtrate of LWW in the present study. This higher removal rate of TOC might be explained by the relatively high fraction of refractory compounds in the dissolved organic carbon part of LWW filtrate (Daghrir et al., 2014; Sumisha et al., 2015) than colloidal particles or suspended solids generated through electrocoagulation.

It can be seen from Fig. 1b that the TOC removal efficiency of NP-SW stabilized after 30 min despite the absence of additional organic matter which could interfere with NPs oxidation. This means before 30 min, longer aliphatic acid by-products formed from the gradual cleavage of benzene rings and accumulated in the medium. This would have finally allowed it to evolve to short-chain aliphatic acids and reach complete mineralization (Dos Santos et al., 2020). After 30 min, short-chain carboxylic acids presented slower reaction kinetics (Dos Santos et al., 2020; Ouarda et al., 2020). It is important to notice that after 30 min, there was only less than about 30% of NPs remained in the NP-SW solution. This indicated the formation of acids and their mineralization rate became equal (Dos Santos et al., 2020). However, for LWW samples, TOC removal efficiencies do not stabilize even after 60 min, especially for effluents with relatively high initial TOC. Consequently, the low TOC removal rate might be ascribed to a relatively low treatment time.

3.3. EEM fluorescence spectra analysis

Fluorescence spectral characteristics of dissolved organic matter (DOM) during electrolysis were investigated using 3D EEM analysis to explore the destruction mechanisms of NPs in LWW. The EEM fluorescence spectra of synthetic water and LWW before and after spiking as well as during the electrolytic treatment are illustrated in Fig. 2. The reference peaks observed for spiked LWW were identified by comparing their fluorescence properties (excitation/emission (Ex/Em)) with those identified in standard dilutions of NPs (Figure not shown) and pure compounds, such as aromatic protein, tryptophan protein, humic and fulvic acid-like (Chen et al., 2003). For NPs synthetic solution, the first main peak was located at the Ex range of 200–220 centered at Em 300 nm (Peak A), and the second was observed at the Ex/Em of 200–220/250 nm (Peak B) (Fig. 2a). The two peaks located had been reported as protein-like peaks, in which the fluorescence was associated with aromatic protein-like substances. A spot of fluorophores with high fluorescence intensity (FI) was presented in the region of Em > 380 nm. That represented fulvic acid-like substances for the region of ex 200–250 nm and 250–450 nm as humic acid-like substances (Chen et al., 2003). It could represent the presence of surfactants in standard chemicals. The obtained fluorescence spectral map of NPs doped LWW clearly shows two maximum peaks A and B located at the same Ex/Em. (Fig. 2b (2) and 2c (2)). It is important to notice that the initial fluorescence spectral map of LWW without NPs doping presented a peak (Ai) centered at 250/300 (Ex/Em) for both sampled wastewaters S1 and S2 (Fig. 2b (1), 2c (1)). Consequently, initial peak A for doped effluents was the combination between LWW initial aromatic compounds and polystyrene benzene molecules. These features of the fluorescence spectrum have been attributed to the emission from molecules formed between pendant phenyl groups (Torkelson et al., 1981). Thus, the correlation between NPs fluorophores intensity and concentration cannot be adequately established for LWW. By referring to the 3D EEM spectrum of non-fluorescent NPs obtained in our previous works, peak A seems the most suitable reference for polystyrene molecules.

EEM spectra of DOM from NP-spiked waters (NP-SW, NP-S1, and NP-S2) after electro-peroxidation treatment is illustrated in Fig. 2. It can be seen that even initial DOM from LWW, aromatic protein-like seem completely disappear from the waters after 40 min. From the EEM map, humic acid-like degraded after 20 min, aromatic proteins-like after 40 min and fulvic acid-like remained present for up to 60 min. The fast decrease of humic acid-like and aromatic proteins-like was observed because of the degradation and mineralization of these compounds where aromatic structure reacts quickly with $^{\bullet}OH$, active chlorine, and $SO_4^{\bullet-}$ (Garcia-Segura et al., 2015; Luo et al., 2018). More precisely, the intensity of the peaks was followed during electrolysis at the excitation of 215 nm selected (Fig. S2), and peak intensity ratios are displayed in Table S3 which could be used for semi-quantitative analysis. It can be seen in Table S3 that throughout the electro-peroxidation process, the FI (fluorophore intensity) of peaks A and B progressively decreased from 701 to 57 and from 674 to 49, respectively for NP-SW. In addition, Fluorophore initially located between emission 380 and 600 nm was narrowed to 410–500 nm and its intensity decreased. The ratio between the average FI of spot and FI of peak A increased markedly throughout treatment from 0 to 40 min for synthetic water, i.e., FI of peak A decreased. The higher increase in ratio indicates the attack on aromatic protein-like substances (Peak A) was more rapid in synthetic water than in LWW. However, for LWW the ratio decreased after 20 min treatment time, corresponding to a rapid decrease in average FI of spots compared to FI of peak A. The decrease in ratio suggests the degradation of fulvic acid-like is predominant after 20 min given humic acids-like were

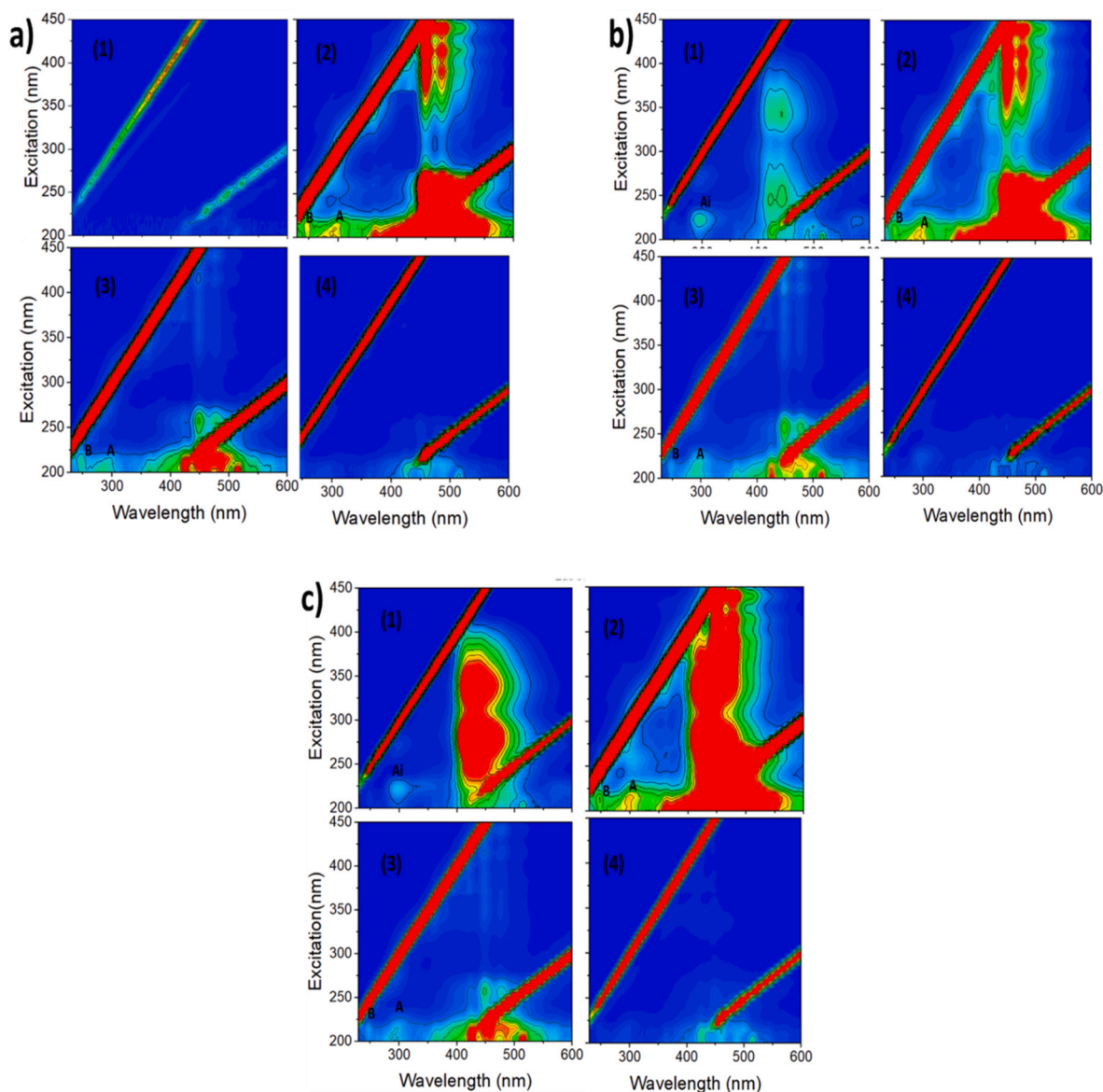


Fig. 2. EEM fluorescence spectra of a) NP-SW, b) NP-S1, and c) NP-S2 samples. (1) Distilled water (a) or LWW (b and c), (2) Spiked sample a $t = 0$, (3) $t = 20$ min, and (4) $t = 40$ or 60 min.

degraded during 0–20 min treatment time. Compared to residual TOC, there was no agreement between the efficiency of TOC removal and the fluorophore intensity remaining after 40 min treatment for effluents. That suggests less short-chain acid accumulated in the DOM has no fluorescence characteristics. Otherwise, that could also confirm fluorescence intensity being dependent on the molecular weight (Ishii et al., 1978).

3.4. Analysis and optimization of operating parameters

During the treatment process, reactive oxygen species such as hydroxyl radicals ($\cdot\text{OH}$), hydrogen peroxide (H_2O_2), and persulfates ($\text{S}_2\text{O}_8^{2-}$) were simultaneously electro-generated. NPs and initial organic compounds were mainly oxidized on the BDD surface by (i) $\cdot\text{OH}$ from water discharge and (ii) $\text{SO}_4^{\cdot-}$ via $\text{S}_2\text{O}_8^{2-}$ reaction with $\cdot\text{OH}$ for the electro-oxidation process. Organic compounds were additionally degraded by $\cdot\text{OH}$ formed from H_2O_2 direct decomposition as well as $\text{SO}_4^{\cdot-}$ generated from $\text{S}_2\text{O}_8^{2-}$ direct reaction with H_2O_2 . H_2O_2 dissociation increased in the range of temperatures ranging from 30 to 40 °C (Özcan et al., 2008). In the present study, the experiments were performed with

initial temperatures varying between 13 and 14 °C, whereas the temperatures ranging between 20 and 30 °C were recorded at the end of the electrolysis, depending on the current intensity applied and the supporting electrolyte (Na_2SO_4) concentrations. Accordingly, in this work, in-situ electro-generated H_2O_2 plays a critical role by increasing hydroxyl radicals and sulfate radicals in the solution, via persulfate activation. It was reported that $\text{SO}_4^{\cdot-}$ attacks organic compounds by electron transfer, however $\cdot\text{OH}$ oxidizes them mainly by H-abstraction after bringing unsaturated bonds (Cai et al., 2018; Lan et al., 2017). Also, $\text{SO}_4^{\cdot-}$ has a longer lifetime (30–40 μs) than $\cdot\text{OH}$ (20 ns) (Nidheesh & Rajan, 2016). The formation of mediated oxidation compounds is more effective than $\cdot\text{OH}$. (Divyapriya and Nidheesh, 2021).

3.4.1. Effect of the experiment parameters on the NP degradation using the experimental factorial design methodology

Four parameters were studied by using a factorial design matrix (2^4): current density (X_1), Na_2SO_4 concentration (X_2), electrolysis time (X_3), and LWW initial TOC concentration (X_4). The influences of these parameters on the efficiencies of NP and TOC removal were investigated. The experimental design and results are summarized in Table S2. Y_{NP}

represents the degradation efficiency of NP and Y_{TOC} represents the degradation efficiency of TOC. X_1 , X_2 , X_3 , and X_4 represent the coded variables (-1 or $+1$) of the principal parameters. The estimations of the effects of the principal parameters are given by the coefficients associated with each parameter. X_1X_2 , X_1X_3 , X_1X_4 , X_2X_3 , X_2X_4 , and X_3X_4 represent the interactions between the principal factors, and their effects are estimated by the coefficients corresponding to these interactions. The experimental response is represented by a linear polynomial model with interactions (see equations (9) and (10)). The coefficients of the polynomial model were calculated using Design-Expert Program Software (Design Expert 7, 2007, Sate-Ease Inc., Minneapolis):

For NP removal:

$$Y_{NP} = 56.07 + 8.91X_1 + 10.07X_2 + 10.23X_3 - 27.09X_4 + 0.53X_1X_2 + 0.04X_1X_3 + 0.81X_1X_4 - 0.02X_2X_3 + 0.93X_2X_4 - 0.61X_3X_4 \quad (13)$$

For TOC removal:

$$Y_{TOC} = 26.81 + 6.40X_1 + 6.32X_2 + 6.72X_3 - 1.29X_4 + 2.12X_1X_2 + 1.72X_1X_3 + 0.94X_1X_4 - 2.05X_2X_3 - 0.91X_2X_4 - 0.87X_3X_4 \quad (14)$$

From Equation (13), it can be seen that the degradation of NP is very influenced by the initial TOC concentration in LWW (X_4 coefficient = -27.09) having a negative effect on the response. The percentage of NP degradation decreased on average by 54.2% ($2 \times 27.1\%$) when the initial TOC concentration in LWW goes from Low (16 mg/L) to high (52 mg/L). The second most important parameter affecting NP degradation is the electrolysis time (X_3 coefficient = $+10.23$) having a positive effect. The increase in the electrolysis time (from 28 to 52 min) contributes to an increase in the percentage of NP degradation on average of 20.5% (2×10.23). The effects of the supporting electrolyte (Na_2SO_4) concentration (X_2 coefficient = 10.07) and the current density (X_1 coefficient = 8.91) are quite similar to this recording with electrolysis duration. Considering the interaction terms, X_2X_4 (Supporting electrolyte concentration and initial TOC concentration) and X_1X_4 (current density and initial TOC concentration) have the most important coefficients ($+0.93$ and $+0.81$, respectively), both interaction effects being positive.

From Equation (14), it can be seen that the current density (X_1 coefficient = $+6.40$), the supporting electrolyte (X_2 coefficient = $+6.32$), and the electrolysis time (X_3 coefficient = $+6.72$) are the most important parameters affecting positively the TOC removal and having approximately equal levels of influence. For instance, the increase in the electrolysis time (from 28 to 52 min) contributes to the increase in the percentage of TOC removal by 13.4% (2×6.72). However, the effect of the initial TOC concentration (X_4 coefficient = -1.29) is relatively weak and its effect is negative. Considering the interaction terms, X_1X_2 (current density and supporting electrolyte concentration) and X_1X_3 (current density and electrolysis duration) have the most important coefficients ($+2.12$ and $+1.72$, respectively), both interaction effects being positive. The contribution of each factor can be calculated using the following equation (15) based on Pareto analysis (Myers et al., 2018) (Fig. S3):

$$P_i = \left(\frac{b_i^2}{\sum b_i^2} \right) \times 100 \quad (i \neq 0) \quad (15)$$

b_i represents the coefficient associated with each factor i . It represents the estimation of the principal effect of factor i . The contributions of the principal effects (X_1 , X_2 , X_3 , and X_4) on the percentage of NP degradation are 7.38%, 9.43%, 9.72%, and 68.23%, respectively. The contribution of the interaction effects (X_2X_4 , and X_1X_4) on the percentage of NP degradation are 0.08% and 0.06%, respectively.

It can be interesting to analyze the interaction X_2X_4 having the most important contribution among the interaction terms (for NP degradation). The interpretation of the interactions X_2X_4 can be facilitated by analyzing Fig. S4. This figure represents a combination of the supporting electrolyte concentration and the initial TOC level. In this figure, the

value of 92% is obtained by calculating the average of the experimental results from the experiments performed with a low level of TOC concentration (16 mg/L) and in the presence of 0.025 mol/L of Na_2SO_4 (experiments 2, 4, 6, and 8). When the level of initial TOC concentration (variable X_4) is fixed at the lowest level (16 mg/L of TOC), the supporting electrolyte (X_2) influenced the response, the average percentage of NP degradation passed from 74 to 92%. However, if the initial TOC concentration is fixed at the highest level (52 mg/L), the supporting electrolyte concentration continues to influence the response, but it is more important than the first case while imposing a low level of initial TOC concentration. The percentage of NP degradation passed from 18% to 40%. Consequently, it can be noticed that the effect of supporting electrolyte concentration is not constant; it depends on the type of the initial TOC concentration. The degradation rate of NP passed from 40% to 92% (gaining 52% for NP degradation) when the supporting electrolyte concentration is fixed at the highest level (0.025 mol/L). When Na_2SO_4 is fixed at the lowest concentration (0.009 mol/L), the degradation rate of NP increased from 18% to 74% (gaining 56% for NP degradation). Consequently, the level of initial TOC concentration is a major factor that influences the degradation rate of NPs but it directly depends on Na_2SO_4 concentration.

3.4.2. Optimization conditions for NP degradation using central composite design methodology

A central composite matrix (Haaland, 1989) was used to optimize the degradation process in all experimental regions. Three quantitative factors (A, B, and C) and one categorical factor (D) were used. The experimental matrix includes a factorial matrix (described above) and sixteen additional experiments carried out at the center of the experimental domain and around the central point of the experimental domain. A set of eight additional experiments were required for each categorical factor (low level of TOC and high level of TOC). A total of thirty-two experiments were carried out to describe the response surface modeling. According to the results presented in Table 2, the response can be described by the polynomial model (quadratic model) from the following equations:

NPs removal (%)

$$\begin{aligned} = & 53.35 + 11.05X_1 + 11.26X_2 + 11.29X_3 - 26.77X_4 + 1.05X_1^2 - 0.87X_2^2 \\ & + 1.63X_3^2 + 0.545X_1X_2 + 0.022X_1X_3 + 1.77X_1X_4 - 0.007X_2X_3 \\ & + 0.254X_2X_4 + 0.1083X_3X_4 \end{aligned} \quad (16)$$

TOC removal (%)

$$\begin{aligned} = & 28.92 + 6.29X_1 + 6.55X_2 + 6.87X_3 - 0.53X_4 - 0.31X_1^2 - 0.90X_2^2 - 0.67X_3^2 \\ & + 2.12X_1X_2 + 1.72X_1X_3 + 0.85X_1X_4 - 2.05X_2X_3 - 0.32X_2X_4 - 0.90X_3X_4 \end{aligned} \quad (17)$$

According to equation (16), the initial TOC concentration is the most important parameter that influences NP degradation. It has a negative effect on NP degradation. An increase in initial TOC concentration decreases the electrochemical degradation of NP. There are competitive reactions between NP degradation and TOC removal during electrolysis. When the initial TOC concentration increases, the fraction of current intensity used for TOC oxidation increases so that NP degradation decreases.

Fig. S5 compares the actual (measured from experiments) and predicted values of NP degradation and TOC removal. The actual and predicted values of NP degradation (and TOC removal) fitted very well. The data are in accordance with the statistical significance of the quadratic model presented in Table S4.

Table S4 presents the analysis of variance (ANOVA) of regression parameters of the predicted response models for NPs, TOC removal, and energy consumption. Considering the low probability values (P-values <0.0001), all the models were significant at a 5% confidence level

Table 2

Central composite matrix and experimental results.

	Experimental design			Experimental plan			Degradation % and Energy consumption		
	X1	X2	X3	A (mA/cm ²)	B (mol/L)	C (min)	NP removal (%)	TOC (%)	Energy (kWh.m ⁻³)
Low-level TOC (D)									
17	-1.67	0	0	12.05	0.017	40	59.71	20.81	6.60
18	1.67	0	0	36.12	0.017	40	96.61	38.98	39.53
19	0	-1.67	0	24.09	0.004	40	46.67	12.90	30.07
20	0	1.67	0	24.09	0.030	40	92.56	34.30	19.23
21	0	0	-1.67	24.09	0.017	20	60.73	15.68	10.43
22	0	0	1.67	24.09	0.017	60	100	42.70	29.67
23	0	0	0	24.09	0.017	40	94.43	27.80	20.13
24	0	0	0	24.09	0.017	40	90.43	27.80	20.13
High-level TOC (D)									
25	-1.67	0	0	12.05	0.017	40	3.04	15.34	5.08
26	1.67	0	0	36.12	0.017	40	60.77	38.45	31.0
27	0	-1.67	0	24.09	0.004	40	8.90	17.41	23.60
28	0	1.67	0	24.09	0.030	40	50.21	42.28	15.67
29	0	0	-1.67	24.09	0.017	20	9.63	15.27	8.83
30	0	0	1.67	24.09	0.017	60	56.28	35.87	21.40
31	0	0	0	24.09	0.017	40	18.77	29.93	15.17
32	0	0	0	24.09	0.017	40	10.63	29.93	15.33

(Hilles et al., 2016). The coefficients of determination obtained in this study for the NPs, TOC removal, and energy consumption ($R^2 = 0.9814$, 0.9921, and 0.9507, respectively) were all higher than 0.80 which represent a good agreement between the calculated and experimental results (García-Gómez et al., 2014). In addition, ANOVA analysis showed the adjusted R^2 is close to 1 ($R^2 = 0.9521$, 0.9795, and 0.9150, respectively).

To determine the optimal conditions for NP degradation and TOC removal in terms of cost and effectiveness, energy consumption needs to be considered. The criteria selected for the optimization conditions were the following: (a) The removal efficiency of NP and TOC has to be maximized with the highest importance (with a minimum of 80% of NP degradation imposed) and (b) the energy consumption should be minimized with lesser importance to reduce the treatment cost related to the consumption of energy. Accordingly, the optimal conditions proposed by the Design Expert software were the following: 31.2 mA/cm² current density, 0.025 mol/L [Na₂SO₄], 52 min treatment time, and 52 mg/L initial TOC. Under these conditions, the model predicts NPs and TOC removal efficiencies near 79% and 48% respectively, and energy consumption of 38 kWh.m⁻³ (Table 3). For comparison, the predicted NPs and TOC removal efficiencies and energy consumption for 16 mg/L initial TOC, were near 100% and 46% respectively and 37 kWh.m⁻³ under the same optimal conditions. To get closer to the reality of the initial TOC load of LWWs in general, 52 mg/L initial TOC was considered for experimental control. So, the prediction for 52 mg/L initial TOC was experimentally validated and the obtained results were $81 \pm 5\%$ NP removal, $43 \pm 3\%$ TOC removal, and 34 ± 0.5 kWh.m⁻³ energy consumption which are close to the predicted values. The treatment cost (including energy and Na₂SO₄ consumption) was 3.05 US \$/m³. To reduce energy consumption, the electrochemical treatments could be done at an initial temperature higher than 20 °C.

Table 3

Optimal conditions determined by Design Expert Program software for NP degradation.

Test number	Factors				Predicted responses			Experimental responses		
	U _A mA/cm ²	U _B mol/L	U _C min	U _D	NP removal (%)	TOC removal (%)	Consumed energy (kWh m ⁻³)	NP removal (%)	TOC (%)	Consumed energy (kWh m ⁻³)
33	31.2	0.025	52	High TOC	79	48	38	81 ± 5	43 ± 3	34 ± 0.5
34	31.2	0.025	52	Low TOC	99	46	37	–	–	–

3.5. Toxicity analysis

To estimate the acute toxicity of the effluents before and after electrochemical treatment, three samples were subjected to analysis: i) Untreated LWW without NP addition; ii) Untreated LWW NP-spiked samples, and; iii) Treated LWW NP-spiked samples. The optimal conditions (described above) were applied for the treated LWW NP-spiked samples (current density of 31.2 mA/cm², concentration of supporting electrolyte of 0.025 mol/L and treatment time of 52 min). Fig. 3 presents the toxicity evaluation. The mortality percentage of *Daphnia*

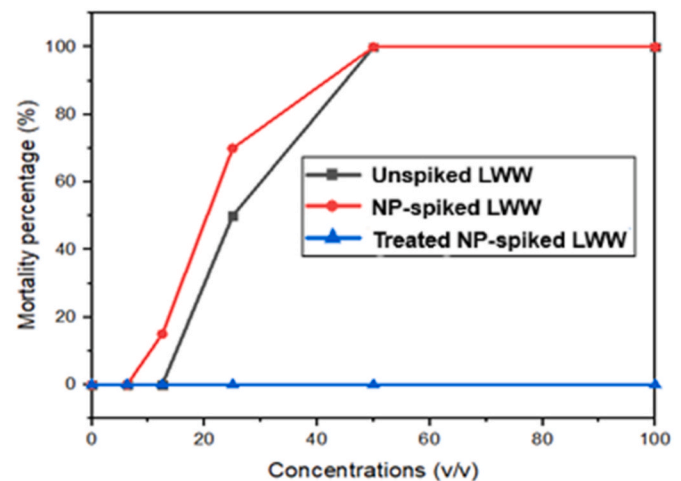


Fig. 3. Toxicity assessment on *Daphnia magna* for untreated and treated NP-spiked LWW samples.

magma against the concentration of LWW was plotted (before and after treatment). The toxicity was not measured for the treated LWW NP-spiked samples ($LC_{50} > 100\%v/v$). By comparison, LWW NP-spiked samples (without treatment) show toxicity at relatively low concentrations ($LC_{50} < 12\% (v/v)$), whereas toxicity was measured at concentrations $LC_{50} < 22.5\% (v/v)$ for untreated LWW samples without NP addition. This means that the addition of NP in LWW contributed to the increase in toxicity in untreated LWW. However, when LWW artificially contaminated by NP of polystyrene was subjected to electrochemical treatment, the toxicity disappeared owing to the degradation/mineralization of toxic compounds. The compounds such as proteins-like (polystyrene NPs and nonylphenol) and humic acids-like compounds could be oxidized to non-toxic by-products. It has been reported by previous studies (García-Gómez et al., 2016; Yassine et al., 2018), relating to electro-oxidation treatment of certain pollutants, an increase in *Daphnia magna* toxicity of treated water. That would be due to the formation of toxic byproducts or attributed to the residual concentration of oxidants generated during the electrolytic treatment. While in our study a decrease in toxicity was obtained. Consequently, optimum operating conditions made it possible to obtain enviro-friendly treated water.

4. Conclusion

Since plastic particles in LWW are a major source of MPs and NPs in wastewater treatment plants, their removal at source is a promising approach to avoid further pollution of water resources. In this work, electro-peroxidation is studied as a process to degrade NPs in industrial LWW. Analysis of the rate of NPs removal revealed that naturally present ions in the LWW increased the rate of NPs degradation and a complete removal could be obtained after 40 min. However, the rate of TOC removal in industrial LWW was lower than that recorded in SW because of the higher initial TOC concentration. 3D EEM analysis suggested that humic acid-like, aromatic proteins-like, and fulvic acid-like compounds could degrade after 20, 40, and 60 min of treatment, indicating the possibility of degrading intermediates by-products that would be generated from NPs. Central composite design was subsequently applied to determine the optimal conditions taking into account both responses of NP degradation and TOC removal. A current density of 31.2 mA/cm^2 , 0.025 mol/L of Na_2SO_4 , and 52 min of treatment time were determined as optimal conditions to minimize energy consumption. Under these conditions, $81 \pm 5\%$ of NP and $43 \pm 3\%$ of TOC could be simultaneously removed for a total cost of $3.05 \text{ US\$m}^{-3}$ of treated LWW. This study showed that the electro-peroxidation of NPs is a promising approach to degrade NPs in industrial LWW. However, the effluent is suggested to be concentrated before electro-peroxidation treatment to enhance the cost-effectiveness of the process.

Authorship statement

Marthe Kiendrebeogo: Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Visualization. Yassine Ouada: Conceptualization, Methodology, Validation, Writing – original draft, Writing – review & editing, Supervision. M.R. Karimi Estahbanati: Conceptualization, Methodology, Validation, Writing – original draft, Writing – review & editing, Supervision. Patrick Drogui: Conceptualization, Methodology, Validation, Investigation, Resources, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. RD. Tyagi: Conceptualization, Methodology, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

All authors have participated in (a) conception and design, or

analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

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Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2023.139963>.

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