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Electrochemical detection and simultaneous removal of endocrine disruptor, bisphenol A using a carbon felt electrode

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ABSTRACT

2,2-Bis (4-hydroxyphenyl) propane (bisphenol A) is a precursor in many industrial and manufactural resins, plastics, and polycarbonate, as well as an endocrine disruptor in humans and animals. Therefore, the real-time sensing and in-situ removal of BPA are in strong demand. This study evaluated a method for the electrochemical detection of BPA using a carbon felt electrode. BPA was detected by cyclic voltammetry. During detection, the BPA was electropolymerized to a non-conductive lump and layer on the electrode surface. Simultaneously, the capacitance and electrochemical properties of the carbon felt decreased. The peak current and BPA concentration showed a linear correlation; the estimated detection limit was 4.78×10^{-7} M. The BPA-electropolymerized carbon felt could be regenerated successfully by ultrasonication. The detection and quantification of BPA in real water samples showed satisfactory recoveries of 98.4–101.0%. The carbon felt-based electrochemical analysis exhibited high sensitivity and reusability, making it applicable to the in-situ and on-site detection and removal of endocrine disruptors, such as BPA.

1. Introduction

2,2-Bis-(4-hydroxyphenyl) propane (bisphenol A, BPA) is a raw material of polycarbonate (PC), polyacrylate, and polysulfone syntheses in the production of food containers, water bottles, cans, and microwave ovenware [1]. BPA is popular in industry and society, but it can be discharged easily into the environment through water flow. BPA is a well-known endocrine disruptor in humans and animals, and it has been reported that BPA may interfere with many biological functions [2]. BPA contains a phenolic group with a similar molecular structure to endocrine hormones, such as estradiol and diethylstilbestrol, with an affinity to estrogen binders. Therefore, it is harmful to human health, even at low concentrations [3]. For example, 1 nM of BPA can interfere with the adiponectin function in human adipose tissue [4], leading to diabetes, cardiovascular disease, and habitual miscarriage in women [5].

The in-situ and ex-situ detection of BPA has been of great interest. BPA can be analyzed quantitatively and qualitatively by gas chromatography–mass spectrometry (GC–MS) and high-performance liquid chromatography (HPLC) [6]. Sun et al. examined the level of BPA contamination in human breast milk and reported a detection limit of 0.48 μM by HPLC [7]. Such ex-situ methods, however, are time-consuming and require complicated sample preparation and pretreatment, which hinder rapid and cost-effective detection and control.

The electrochemical detection of BPA has been suggested for rapid and high sensitivity and low-cost application for unrestricted use and location [8–10]. When an electrochemical method is implemented, it is important to select a material for the working electrode. A range of carbon materials with complex synthetic fabrication have been evaluated for the development of an appropriate working electrode to improve the electrical sensitivity for BPA detection [11,12]. The electrochemical BPA detections from real water samples were carried out in the previous works. Zou et al. fabricated GNP-AuNPs/GCE electrode, which can detect BPA at 27 μM in real water samples [13]. Jemmeli et al. also reported the first example of a paper-based electrochemical device (CB/uPAD) to detect BPA at 0.03 μM in river and drinking water samples without additional treatment [14].

However, the problem of conventional electrochemical methods was a deactivation of the carbon electrodes after electrochemical detection of BPA due to the formation of a polymeric product on the carbon surface. Agüí et al. detected phenolic compounds and reported that the properties of the metal and carbon surface changed to non-conductive or fouled

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during electrochemical operation with BPA, making them unusable for further analysis [15]. When a poised potential was applied to BPA, the electrochemical oxidation of phenolic compounds proceeds, and allows phenoxy radicals to be transformed to quinone compounds, such as hydroquinone and benzoquinone [16,17]. In an alternative route, phenoxy radicals undergo a coupling reaction followed by polymerization. Depending on the type and number of substituents in the aromatic ring of the phenol derivatives, potential phenoxy radicals, such as ether and quinine-like oligomeric compounds, are supposed to lead electropolymerization on an electrode and prevent further electrochemical reaction [16,17].

Various reusable processes can be implemented to regenerate the spent carbon electrode. The common techniques for the regeneration are chemical extraction, mechanical extraction, and bio-regeneration. However these methods have drawbacks, such as high energy and chemical consumption and operating cost. Recently, ultrasonic treatment has been reported to remove contaminants and fouling from an electrode surface [11,18–21].

This paper presents the electrochemical detection of BPA using carbon felt without a complicated electrode synthesis and fabrication. The oxidation/reduction reactions of BPA and concomitant removal from the solution occur at the interface between the carbon felt surface and the electrolyte [22]. Cyclic voltammetry was performed at different BPA concentrations and surface areas of carbon felt. The electrical capacitance and redox sensitivity have been used as indicators for quantitative analysis. Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), Fourier transform infrared (FT-IR) spectroscopy, and Raman spectroscopy were carried out to examine the morphology and functional groups of the carbon surface by electropolymerization. The electrochemical detection method was applied to real tap and bottled water samples. The removal of the BPA film by ultrasonication and reuse of the carbon felt was examined.

2. Experimental

2.1. Reagents and apparatus

BPA (2,2-bis (4-hydroxyphenyl) propane, 97%) was purchased from Sigma Aldrich. A stock solution was prepared by dissolving BPA in methanol (50 mg/ml final) and diluted to the appropriate concentration for testing. The electrolyte was a phosphate buffer solution (0.1 M) containing 1 M KH_2PO_4 and 1 M K_2HPO_4 that was adjusted to pH = 7.0 with NaOH or HCl. Aqueous solutions of Na_2SO_4 (0.2 M) and potassium ferrocyanide (4 mM in final) were used as electrochemical markers for redox and capacitance analyses. All other solvents and chemicals were of analytical reagent grade. Distilled water and deionized water from a Millipore Milli-Q system were used to prepare all the solutions and electrolytes. In some experiments, real water samples, such as untreated tap and bottled water supplemented with BPA, were used as the spiking experiment, as reported previously [13]. The samples were measured in triplicate with the relative standard deviation (RSD).

The surface morphology and elemental distribution of the carbon felt surface after BPA electropolymerization was analyzed by SEM (VEGAII LMU, Tescan, Czech). For sample preparation, the carbon felt was sliced to 1 cm × 1 cm pieces using a razor knife and dried overnight in a freeze dryer (FD8508, Ilshin). The prepared electrode samples were coated with gold nanoparticles using a sputter coater (E-1010, Hitachi). The SEM image was obtained at 10 kV. The functional groups and chemical/molecular changes in the surface were examined by FT-IR (Spectrum GX, PerkinElmer) spectroscopy in attenuated total reflection (ATR) mode between 4000 and 650 cm^{-1} with 64 scans and a Raman spectrometer (NRS-5100, JASCO) with a 532 nm excitation laser wavelength with 20 s integration time.

The electrochemical analyses were examined by cyclic voltammetry (CV) in a three-electrode system. The scan rate of CV was 20 mV/s, and multiple cycles were carried out to obtain the average response of the peak current and capacitance. The electrochemical activity of the carbon felt electropolymerized by BPA, was examined using redox and capacitance markers, such as potassium ferrocyanide and sodium sulfate respectively [23]. Sonication (40KHz, POWER SONIC405, Hwashin Instrument, Korea) was carried out to remove the electropolymerized BPA layer from the carbon felt and reactivate the electrochemical activity of the surface. A carbon felt electrode was placed in distilled water, sonicated for two hours at 25 °C, and then stored in an oven for one day before the experiment. The capacitance of the electrode was determined using the following formula.

$$C = \int I \, dV / (\nu \cdot m \cdot V) \tag{1}$$

where I, V, ν, and m are the current density (A/cm^2), potential, scan rate (mV/s), and mass of the electrode (g), respectively [24].

2.2. Electrochemical detection and removal of BPA

A single chamber type electrochemical cell was used with a carbon felt electrode (thickness 6.5 mm, C200–2911, US Fuel Cell Store, USA) as the working electrode and a graphite rod (GR002H) as the counter electrode. An Ag/AgCl (3 M KCl) electrode was used as the reference electrode. All experiments were performed with a phosphate buffer solution (0.1 M, pH 7.0). The electrolyte was stirred using a magnetic stirrer. The voltage and current measurements were taken using a Potentiostat (VersaSTAT 3, AMETEK, USA) and Versa StudioTM software (AMETEK, USA). The oxidation/reduction peaks of BPA were detected by CV with a scan range of −0.2 V to 0.8 V (vs. Ag/AgCl) at a scan rate of 20 mV/s. Chronoamperometry method was used to remove BPA from the solution. BPA was electropolymerized on the surface of the carbon felt by applying a constant potential of 0.6 V (vs. Ag/AgCl) to the working electrode (i.e., carbon felt).

The removal of BPA from the solution was confirmed by HPLC (Alliance 2695 system, Waters, USA). The liquid samples were introduced to HPLC equipped with a UV switching valve and quaternary load pump. High-resolution Orbitrap MS was performed on an Exactive8 column (250 × 4.6 mm, 5 μm, Agilent, USA) while maintaining a column temperature at 30 °C. The mobile phase consisted of HPLC grade acetonitrile and water (50:50 ν/v) and was introduced to the column at a flow rate of 1 mL/min. The column effluent was monitored at 271 nm to detect the BPA.

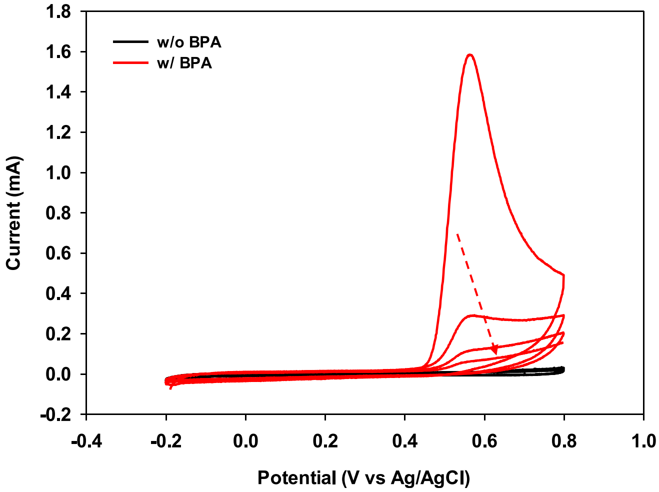

Fig. 1. Continuous CV scan with 0.1 mM BPA in a phosphate buffer solution (pH 7.0) using a carbon felt electrode. The arrow indicates that the scan cycle is increasing.

3. Results and discussion

3.1. Electrochemical properties of BPA

Fig. 1 presents CV traces of the oxidation of BPA (0.1 mM) using a carbon felt electrode. In the forward scan, the oxidation peak appeared at 0.53 V (vs. Ag/AgCl). In contrast, the reduction peak was not identified clearly, probably due to the irreversible electrochemical reaction of BPA on the electrode. The peaks were tended to decrease significantly with successive CV scans. At the same BPA concentration, the carbon felt electrode used (i.e., after multiple CV scans) showed a similar reduction of the peak current. These results suggest that BPA can be detected at the specific potential in the CV scan. BPA is oxidized irreversibly on the electrode surface, preventing further BPA monomer interactions with the electrode.

3.2. Changes in the electrochemical performance of carbon felt by BPA polymerization

The electropolymerization of BPA on the electrodes was investigated in a three-electrode system. Once BPA was polymerized by the oxidative scan of CV, a non-conductive polymer film formed on the carbon surface. The insulating film was due to the formation of phenoxonium ions by the two-electron process when the ring of BPA was oxidized anodically [25–27]. The CO and CC coupling of two phenoxonium ions form a neutral dimer [28]. These reactions are propagated continuously by electrochemically generated BPA monomers, dimers, or oligomers. The resulting electropolymerized BPA is a non-conductive film, which insulates the electrode from the electrolyte so that no further oxidation occurred on the electrode surface.

To identify the insulating film, the redox sensitivity and capacitance of the carbon felt, with and without BPA using redox markers, were compared. Fig. 2 presents the redox sensitivity and capacitance using potassium ferrocyanide and sodium sulfate as markers, respectively. The carbon felt without BPA electropolymerization showed clear redox peak currents (78 mA at 0.43 V and − 148 mA at 0.07 V vs. Ag/AgCl, respectively). In contrast, the electropolymerized carbon felt showed a significant decrease in the oxidation and reduction peak currents (0.03 mA at 0.54 V and − 0.003 mA at 0.47 V vs. Ag/AgCl, respectively) with potassium ferrocyanide (Fig. 2a). The sodium sulfate revealed the significantly reduced capacitance after BPA polymerization. (2.98 F·g^{-1} to 1.28 F·g^{-1}) (Fig. 2b). These results suggest that the electrochemical sensitivity and capacitance were reduced by the non-conductive film produced from electropolymerization. The similar electropolymerization of the BPA monomer on the carbon surface has been reported [29–31].

3.3. Morphological change in carbon felt by BPA electropolymerization

Fig. S1 shows the morphological changes to the surface of carbon felt before and after applying the potential. After electropolymerization, lump structures were observed on the carbon fiber compared to the bare carbon felt. The formation of these localized structures might have resulted from the oxidation of BPA monomer under an oxidative potential during CV. In addition to such lumps, based on the results of Figs. 1 and 2, the polymeric layer might be distributed evenly over the carbon surface, despite not being identified by SEM. The electrical conductivity and active surface of carbon for BPA monomer oxidation decreased significantly due to fouling of the carbon surface. The elemental distribution on bare carbon felt, and BPA-electropolymerized carbon felt showed a considerable difference in the active surface (Fig. S4). Only signals for C and O were observed on the bare carbon felt electrode, whereas the C signal disappeared in BPA-electropolymerized one (Fig. S4a & b). This suggests that the carbon surface is covered by a polymeric layer and lump structures by BPA electropolymerization.

FT-IR spectroscopy was carried out to identify certain functional groups [32] (Fig. 3). No significant peaks were observed in the bare carbon felt electrode. In contrast, the strong peaks near 3300 cm^{-1} and 1640 cm^{-1} with BPA electropolymerized carbon felt were assigned to the stretching vibration of OH and aromatic CC bonds, respectively. An epoxy CO bond and an alkoxy CO bond were observed near 1290 cm^{-1} and 1063 cm^{-1}, respectively [32–34]. Other peaks (2800–3000 cm^{-1} and 650–1800 cm^{-1}) with significantly high intensities were observed in the BPA electropolymerized carbon felt compared to the control [32]. These results suggest that the BPA monomer was electropolymerized on the carbon surface, which resulted in a change in chemical properties.

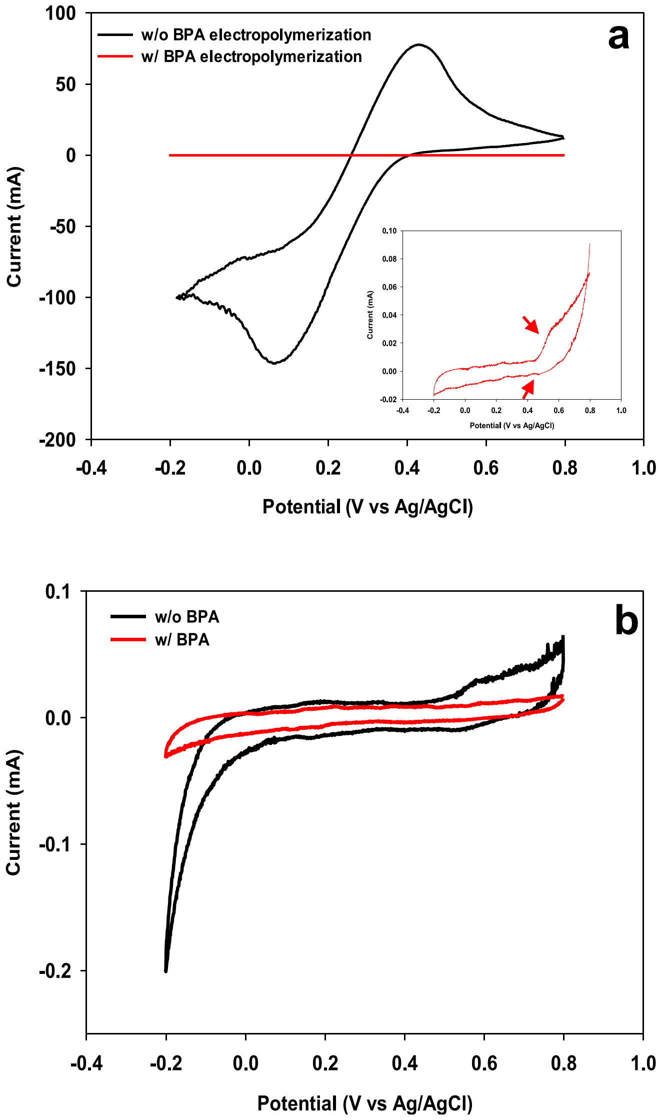

Fig. 2. Comparison of the redox sensitivity and capacitance of carbon felt with and without BPA electropolymerization. (a) with 4 mM potassium ferrocyanide and (b) with 0.2 M sodium sulfate. The inset box shows the result of BPA electropolymerized carbon felt in the range of −0.2 to 0.8 with a magnified y-axis.

Fig. S5 presents the Raman spectra. The carbon felt showed the typical bands of the carbon structure at 1352 cm^{-1} and 1592 $cm^{-1,}$ which were assigned to the D and G bands, respectively. The D band is activated by the presence of defects and is probably associated with the breathing mode of the sp^2 atom. The G band is associated with the dispersion of the first-order phonon, E_{2g} [35]. The 2D band at 2690 cm^{-1} is a second-order process related to a phonon, which is activated by double resonance processes. The ratio of the intensity of the D band and G band (I_D/I_G) is an indicator of the degree of disorder. The I_D/I_G of BPA electropolymerized carbon felt (1.14) was lower than that of bare carbon felt (1.38), suggesting that the electropolymerization of BPA had disordered structures on the surface [13]. The BPA electropolymerized carbon felt exhibited characteristic

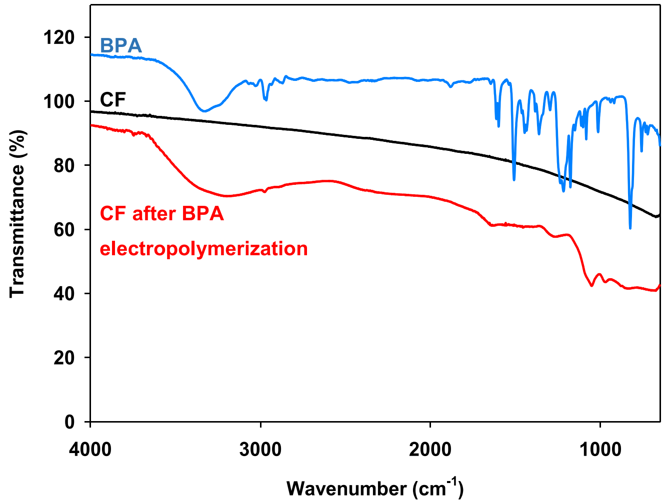

Fig. 3. FTIR spectra of BPA electropolymerized carbon felt (CF) electrodes compared to the bare carbon felt and aqueous BPA monomer.

peaks at 1090 cm^{-1}, 1235 cm^{-1}, 1603 cm^{-1}, and 3317 cm^{-1} [36]. The peaks at 1090 cm^{-1} and 1235 cm^{-1} were attributed to the CH wagging vibration and epoxy CO stretching bands, respectively [37]. The peaks at 1603 and 3317 cm^{-1} were attributed to the invariant aromatic stretching band, phenyl ring stretching, and phenyl-hydrogen stretching modes, respectively [38]. The Raman spectra showed similar results to the FT-IR spectra, indicating electropolymerization on the carbon surface.

3.4. Electrochemical detection of BPA

Fig. 4a shows CV traces at BPA concentrations ranging from 0.01 to 150 μM. The peak current increased with increasing BPA concentration. The inflection point of the BPA concentration was observed at approximately 10 μM, in which the electropolymerization behavior changed. A plot of the peak current as a function of the BPA concentration was linear between 10 and 150 μM. Eq. (2) presents the regression equation at BPA concentrations of more than 10 μM with a detection limit of 0.55 μM. Eq. (3), however, is the regression equation at BPA concentrations below 10 μM with a detection limit of 1 μM. The detection limit was 0.48 μM over the entire range from 0.01 to 150 μM (4) (Fig. 4b).

$$I_{pa}(\mathrm{mA}) = 0.0068C_{BPA}(\mu\mathrm{M}) + 0.1896\ (R^2 = 0.9997) \tag{2}$$

$$I_{pa}(\mathrm{mA}) = 0.0037C_{BPA}(\mu\mathrm{M}) + 0.0221\ (R^2 = 0.9716) \tag{3}$$

$$I_{pa}(\mathrm{mA}) = 0.0078C_{BPA}(\mu\mathrm{M}) + 0.0839\ (R^2 = 0.976) \tag{4}$$

Table 1 lists the reported detection limits in previous studies that examined BPA detection electrochemically. Note that the cost-effective carbon felt electrode, which was fabricated without expensive physical modification or a complicated synthesis process for carbon, showed a comparable detection limit of 0.48 μM to previous studies.

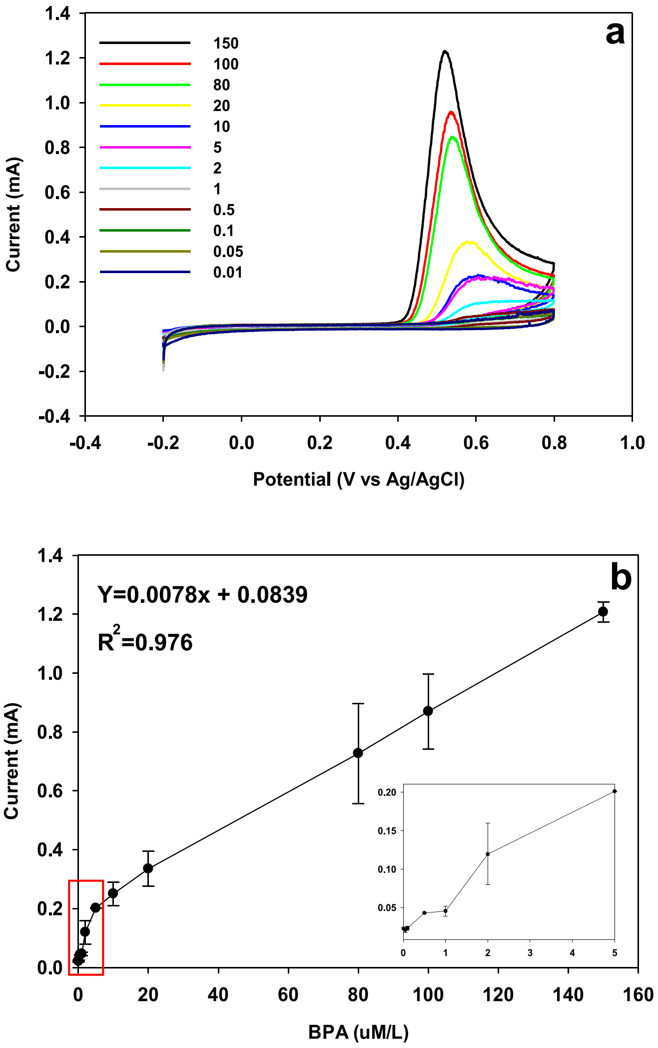

Fig. 4. Changes in the detection peaks according to BPA concentration (a) and detection limit curve (b). The inset graph shows the detection current at BPA concentrations below 5 μM.

Table 1
Comparison with other reports in the literature for detecting bisphenol A using electrochemical analytical methods.

Electrodes	Linear range (uM)	Limit of detection (M)	References
GCE/Fe_3O_4 NPs/Au NPs/Si4Pic$^+$Cl$^-$	0.02–1.4	7 × 10^{-9}	[40]
AuPdNPs/GNs	0.05–10	8 × 10^{-9}	[41]
CoPc /CPE	0.08–12.5	1.0 × 10^{-8}	[42]
SGNF/AuNPs/GCE	0.08–250	3.5 × 10^{-8}	[43]
MCM-41	0.22–8.8	3.8 × 10^{-8}	[44]
MIPPy/GQDs	0.1–50	4 × 10^{-8}	[45]
Pt/Gr–CNTs	0.06–10	4.2 × 10^{-8}	[46]
Graphene/GCE	0.05–1	4.7 × 10^{-8}	[12]
MWCNTs-TiN/GCE	0.1–50	5 × 10^{-8}	[47]
$[Ru(bpy)_3]^{2+}$ on the ITO	5–120	2.9 × 10^{-7}	[48]
Exfoliated graphite (EG)	1.56–50	7.6 × 10^{-7}	[31]
Carbon felt	0.01–150	4.8 × 10^{-7}	This work

3.5. Removal of BPA according to the different surface area of carbon felt

Fig. 5a presents the CV responses of BPA according to the projected surface area of carbon felt from 750 to 1350 mm^2. The peak current increased with increasing surface area (Fig. 5b). On the other hand, the normalized peak current divided by the surface area resulted in a similar level (1.0 ± 0.3 μA/mm^2). This indicates that the electropolymerization of BPA is limited by the area of the carbon felt electrode. Thus, electropolymerization increased further with increasing surface area. Polcaro and Palmas et al. reported the decomposition of chlorophenols electrochemically in an aqueous solution using a porous carbon felt electrode [39]. The ferrocyanide ion was used as a redox marker to examine the sensitivity of a carbon felt electrode during electropolymerization (Fig. S2a). The peak current of the ferrocyanide ion decreased as

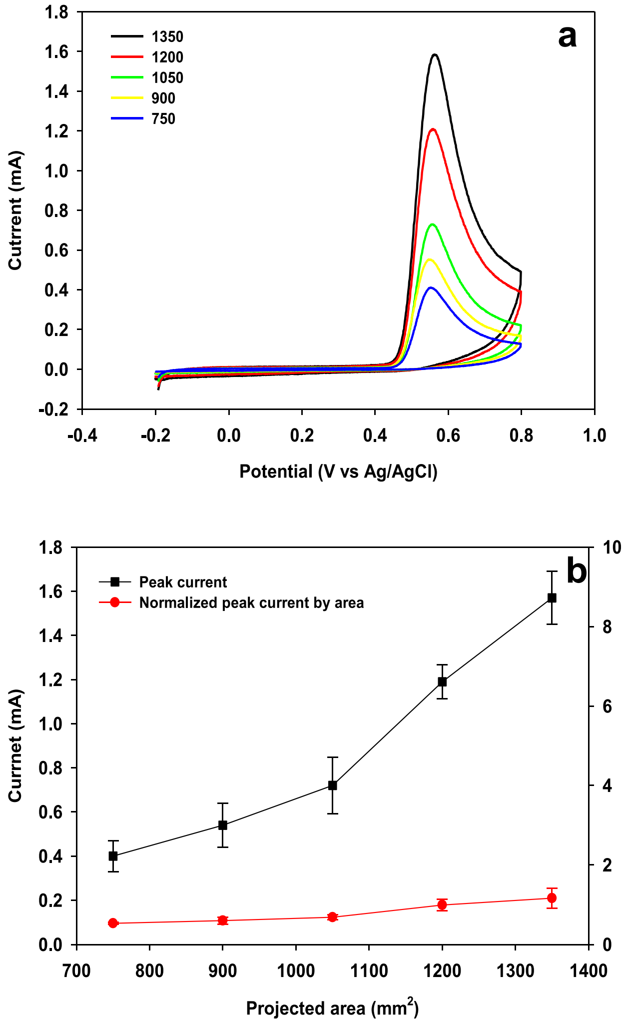

Fig. 5. CV according to the area of the carbon felt electrode (a), peak current and peak current normalized to the area of the carbon felt electrode (b).

electropolymerization proceeded. The optimal potential for the oxidative polymerization of BPA was approximately 0.6 V (vs. Ag/AgCl), in which the BPA monomer could be electropolymerized on the carbon surface. The decrease in peak current of ferrocyanide ions reduced significantly after electropolymerization.

To confirm the removal of BPA from the aqueous phase, HPLC was carried out with different application times at 0.6 V (vs. Ag/AgCl) (Fig. S2b). The removal efficiency with an initial concentration of 0.1 mM BPA increased with increasing treatment time and achieved 80% removal within 30 min. The results of BPA removal (0.1 mM BPA, 80% after 30 min) using cost-effective carbon felt was comparable to that of Kuramitz et al. [23], which used a bundle of 100 strings of carbon fiber by the electrochemical method (0.01 mM BPA, 100% removal after 60 min).

To determine the practical performance and feasibility of carbon felt, the determination of BPA from tap and bottled water samples was examined by spiking experiments. The detection and quantification of BPA were carried out with tap water and bottled water by adding BPA and showed satisfactory recovery values of 98.4–99.3% and 98.9–101.0%, respectively (Table 2). The relative standard deviation (RSD) was 0.43–1.13% and 0.41–0.75%, respectively.

3.6. Regeneration of carbon felt by sonication

The electrochemical activity of carbon felt to BPA polymerization decreased to zero after multiple CV scans. The electropolymerized carbon surface became nonconductive, which prevented further electrochemical detection of BPA in solution, as shown in Fig. 2. On the other hand, the peak current was recovered after ultrasonicating the electropolymerized carbon felt (Fig. 6). Sonication removed the lumps on the carbon fiber produced by the previous electropolymerization, as shown in the SEM image (Fig. S3). Sonication can also regenerate the porous structure and reactivate the carbon surface for BPA oxidation, allowing the reuse of carbon felt for the further removal of BPA. This suggests that porous or fibrous carbon materials can be reused to remove BPA after mechanical disintegration, such as sonication.

Table 2
Detection of BPA in real water samples.

Water sample	BPA added (uM)	Recovery (%)	RSD (%)
Tap water	0	Not detected	–
	0.5	99.2	0.51
	1	99.3	0.43
	2	98.4	1.13
Bottled water	0	Not detected	–
	0.5	98.9	0.75
	1	101.0	0.73
	2	99.4	0.41

3.7. Implication

The electrochemical detection of endocrine disruptors has been highlighted as an in-situ and rapid analysis. The electrochemical sensitivity varies according to the characteristics of the electrode materials, which host electrochemical reactions. Various working electrodes for this purpose have been developed, but they require expensive and non-reusable materials, such as a glassy carbon electrode (GCE) and complicated chemical synthesis methods. Although these electrodes have good analytical features in terms of a wide linear range, high sensitivity, and low detection limits, there is still a problem with the formation of non-conducting films by BPA electropolymerization in the most studies. Many researchers have focused on improving the response signal for BPA detection, either using novel materials or optimizing existing methods. Nevertheless, most of the BPA electrochemical sensors reported easily lose their electroactivity and cannot be reused. In this study, a cost-effective and reusable carbon felt material was implemented for electrochemical detection. Porous carbon could remove BPA from the aqueous phase. A simple sonication treatment regenerated the porous carbon surface and recovered the sensitivity for electrochemical detection. To the best of the authors' knowledge, this is the first report of the in-situ quantitative analysis and removal of BPA using a reusable carbon felt material. The detection limit estimated in this study was

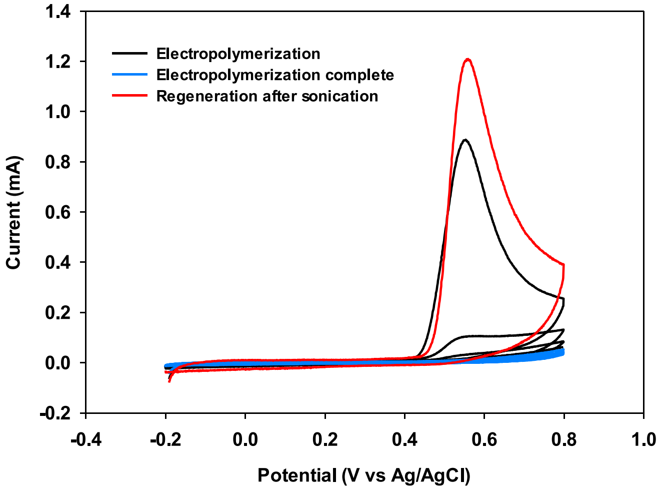

Fig. 6. Regeneration of BPA polymerized carbon felt electrode by ultrasonication.

comparable to the reported value, but detection was achieved using inexpensive and easily obtainable carbon materials. The suggested carbon felt-based analysis was successfully applied to the real water samples. Carbon materials have been used for general drinking and wastewater treatment. Therefore, these studies are expected to contribute to the development of a combined process for the simultaneous detection and removal of endocrine disruptors from real water systems.

4. Conclusions

An inexpensive carbon felt without complex surface modification was implemented for in-situ electrochemical detection and quantitative analysis of BPA. Applying a specific potential (0.6 V vs. Ag / AgCl) using chronoamperometry, 80% of BPA in the solution was removed after 30 min. The estimated detection limit of BPA was 4.78×10^{-7} M, which is comparable to the values reported elsewhere. Once BPA was polymerized by the oxidative potential, a non-conductive polymer film formed on the surface of carbon felt. The BPA-electropolymerized surface could be regenerated and reactivated for detection by ultrasonication. Satisfactory recoveries and relative standard deviations of electrochemical detection were obtained for real water samples. This study contributes to the development of in-situ and on-site analysis and the removal of endocrine disruptor BPA by using a cost-effective carbon felt.

Credit author statement

The investigation, experiment, and writing original draft, Minsoo Kim; Investigation and electrochemical analysis, Young Eun Song.; Bisphenol A detection by HPLC, Jiu-Qiang Xiong; Review methodology and analyses, Kyoung-Yeol Kim and Min Jang; writing, review and editing and funding, Byong-Hun Jeon and Jung Rae Kim.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jelechem.2020.114907.

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