

Article

Fast Removal of Polybrominated Diphenyl Ethers from Aqueous Solutions by Using Low-Cost Adsorbents

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Abstract: 4-Dibromodiphenyl ether (BDE-3) and 4,4'-dibromodiphenyl ether (BDE-15) are two of the major polybrominated diphenyl ethers used as flame-retardant additives in computer main boards and in fireproof building materials. In this study, we evaluated the potential of three low-cost adsorbents, black tea, green tea, and coconut palm leaf powders, to adsorb BDE-3 and BDE-15 from aqueous solutions. The results showed that pressure steam washing of the adsorbents increased their capacities to adsorb BDE-3 and BDE-15. The maximum adsorption capacities of pressure steam-washed black tea, green tea, and coconut palm leaf powders were $21.85 \text{ mg} \cdot \text{L}^{-1}$, $14.56 \text{ mg} \cdot \text{L}^{-1}$ and $22.47 \text{ mg} \cdot \text{L}^{-1}$, respectively. The results also showed that the adsorption equilibrium (q_e) was achieved at 4 min. Moreover, 97.8% of BDE-3 and 98.5% of BDE-15 could be removed by adsorbents pretreated with pressure steam washing. The kinetic data fitted well with a pseudo-second-order equation. The adsorption rate constants (k_2) of all pressure steam-washed adsorbents ranged from 8.16×10^{-3} to $6.61 \times 10^{-2} \text{ g} \cdot (\text{mg} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$, and the amount adsorbed at q_e by all pressure steam-washed adsorbents ranged from 4.21 to $4.78 \text{ mg} \cdot \text{L}^{-1}$. Green alga *Chlorella vulgaris* was used as the test organism and the median effective concentration values of BDE-3 and BDE-15 were 7.24 and $3.88 \text{ mg} \cdot \text{L}^{-1}$, respectively. After BDE-3 and BDE-15 were removed from the solution, their biotoxicities markedly decreased. These findings indicate that these low-cost adsorbents can be used to remove BDE-3 and BDE-15 from aqueous solutions and wastewater.

Keywords: polybrominated diphenyl ethers; adsorption; low-cost adsorbents; biotoxicity assays

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as flame-retardant additives in various industrial products. PBDEs reduce flammability by interfering with the combustion of polymeric materials. PBDEs are structurally similar to polychlorinated biphenyls and polybrominated biphenyls and thus have similar properties. Because the chemical structure of PBDEs closely resembles that of thyroid hormones, PBDEs have been identified as endocrine disruptors that can induce neurodevelopmental deficits and cancer [1,2]. However, the information on their toxicology is extremely limited. Because of their high production and application rates, PBDEs have commonly been found in the environment in the past decade [3–8]. Therefore, the remediation of PBDE-contaminated environments is crucial for lowering their toxicity.

4-Dibromodiphenyl ether (BDE-3) and 4,4'-dibromodiphenyl ether (BDE-15) are two of the PBDEs most widely used as flame-retardant additives. BDE-3 and BDE-15 are extensively detected in the environment because of the degradation of commercial products containing PBDEs. Studies on PBDEs have mainly focused on their environmental degradation. Li et al. [9] reported that 2,2',4,4'-tetrabromodiphenyl ether (PBDE-47) could be photodegraded in nonionic surfactant solutions [9]. Rayne et al. [10] reported that anaerobic biodegradation and photochemical degradation are two preferred remediation mechanisms for PBDEs. Adsorption is another preferred mechanism for remediating PBDE-contaminated environments [11–13]. In the past decade, activated carbon has been the most widely used adsorbent for removing various types of organic pollutants because of its effectiveness and high adsorption capacity. However, its use remains limited because of the high operational costs. Therefore, several researchers have focused on finding low-cost adsorbents. Low-cost adsorbents or nonconventional alternative adsorbents are generally nonhazardous wastes produced from industries, agriculture, or biosorbents. They have been well documented in treating different organic pollutants over the past decade [14–23]. In particular, the use of agricultural wastes in the adsorption system has drawn attention from numerous researchers because (1) these wastes are abundantly available; (2) most agricultural wastes do not require a complex pretreatment step or activation process before application and can be readily used; (3) regeneration of these adsorbents may not be necessary (unlike activated carbon, where regeneration is essential); and (4) less maintenance and supervision are required during the adsorption process. However, the use of these cheaper alternatives in wastewater treatment remains limited because of both insufficient documentation in real wastewater systems and the necessity of post-usage disposal.

Subtropical Taiwan is located at the western edge of the Pacific Ocean and contains numerous subtropical plants and crops such as black tea (BT), green tea (GT), and coconut palm (CT). These plants are widely cultivated in Taiwan and various tropical countries, such as China, India, Thailand, and Indonesia. The leaves of these plants are generally used as a compost material or are burned on site after harvest. The major constituents of these leaves are cellulose, lignin, and hemicelluloses; therefore, some studies have evaluated the application of these subtropical plants and leaves as low-cost adsorbents in wastewater treatment [24–26]. The use of these leaves is doubly beneficial because they are a natural adsorbent and reduce the amount of agricultural waste. Utilization of this waste for wastewater treatment is highly beneficial because it not only converts the waste into a useful material, but also prevents on-site burning of the waste and mitigates disposal costs [27,28].

In this study, we evaluated the potential of BT, GT, and CT leaf powders as low-cost adsorbents for removing BDE-3 and BDE-15 from aqueous solutions. In addition, we investigated the effects of different pretreatments of tea leaf powders, including pressure steam washing, acid washing, and base washing, on adsorption. Furthermore, we determined the biotoxicity of BDE-3 and BDE-15 to the green alga *Chlorella vulgaris* and calculated the adsorption rates of BDE-3 and BDE-15.

2. Materials and Methods

2.1. Chemicals

The molecular weight and chemical formula of BDE-3 are $249.1 \text{ g}\cdot\text{mol}^{-1}$ and $\text{C}_{12}\text{H}_9\text{BrO}$, respectively. The molecular weight and chemical formula of BDE-15 are $328 \text{ g}\cdot\text{mol}^{-1}$ and $\text{C}_{12}\text{H}_8\text{Br}_2\text{O}$, respectively. BDE-3 (100% purity, CAS: 101-55-3) and BDE-15 (100% purity, CAS: 2050-47-7) were purchased from AccuStandard Inc. (New Haven, CT, USA). Individual BDE-3 and BDE-15 stock solutions were dissolved in *n*-hexane to a concentration of $10,000 \text{ mg}\cdot\text{L}^{-1}$ before use. Acetone and *n*-hexane (HPLC grade, $\geq 99.93\%$) solvents were purchased from E. Merck (Darmstadt, Germany). All reagents were of analytical grade. All solutions were prepared using double distilled water.

2.2. Preparation and Characterization of Low-Cost Adsorbents

Black tea (*Clonorchis sinensis*), green tea (*Camellia sinensis*) and coconut palm (*Cocos nucifera*) were used in this study. BT (full fermentation) and GT (not fermented) leaves were obtained from a tea processing factory near I-Shou (University Kaohsiung, Taiwan.), and the CT leaves were collected from the campus. After collection, the leaf samples were first washed with tap water thrice to remove dust and impurities. The leaves were then air-dried and subsequently oven-dried at 80 °C for two days. Prior to use, the dried leaves were powdered using a grinder. According to our previous study and experiment (Weng et al. [29]), adsorbents which passed the ASTM 100 mesh screen (particle size < 0.149 mm) could both have the higher sedimentation coefficient and specific surface area. These characteristics could help to enhance the adsorption capacity and the operation of the adsorption test. Therefore, the leaf powder was passed through an ASTM 100 mesh screen. Particles with a diameter of <0.149 mm were used in adsorption studies.

To characterize the leaf powder, various basic properties were analyzed. The pH of the leaf powder was measured in a water suspension at a 1:1 weight ratio of leaf powder to distilled water by using a pH meter (YK-2005WA, Lutron Electronic Enterprise, Taipei, Taiwan). The pH at zero point of charge (pH_{zpc}) of the leaf powder was determined using a zeta meter (Lazer ZeeR model 500, Pen Kem Inc., Bedford Hills, NY, USA). A Fourier transform infrared (FTIR) spectrophotometer (Spotlight 300, PerkinElmer, Waltham, MA, USA) covering the wavenumber range from 400 cm⁻¹ to 4000 cm⁻¹ was used to identify the chemical constituents of the leaf powder. The gravimetric density of the leaf powder particles was determined according to the methods described in ASTM D854-92. A scanning electron microscope (SEM, Philips 501 scanning electron micrograph; Philips, Eindhoven, The Netherlands) was used to characterize the morphology of the leaf powder.

2.3. Pretreatment of Low-Cost Adsorbents

To evaluate the most effective pretreatment method for BDE-3 and BDE-15 adsorption, the leaf powder was pretreated using acid washing (A-), base washing (B-), and pressure steam washing (S-). These pretreatments were expected to alter the surface physical morphology and major functional groups of the leaf powder. In the acid washing procedure, the leaf powder was immersed in 0.1 M HNO₃ solution for 1 h. In the base washing procedure, the leaf powder was immersed in 0.1 M NaOH solution for 1 h. In the pressure steam washing procedure, the leaf powder was subjected to a high pressure (70 kPa) at 100 °C for 20 min by using a pressure cooker. These pretreatment methods alter the surface functional groups of the leaf powder and remove residual tea color (tannins) and impurities.

2.4. Adsorption Experiments

Adsorption experiments were performed to obtain the maximum adsorption capacity. The experimental procedures are described as follows: (1) all adsorption experiments were done using 125 mL serum bottles containing 99.95 mL sample solution. 0.05 mL of PBDE (BDE-3 or BDE-15) stock solution (10,000 mg·L⁻¹) was added into 99.95 mL sample solution. A series of 100 mL samples of a solution containing 5 mg·L⁻¹ of a PBDE (BDE-3 or BDE-15) was prepared. The PBDEs concentration which is used in this study was referred to several environmental investigation papers [30–32]; (2) either 0.01 or 0.002 g·L⁻¹ of leaf powder was added to the PBDE solution; (3) the bottles were shaken on a reciprocal shaker at 150 oscillations min⁻¹ at room temperature (27 °C) for 80 min; (4) the PBDE solution was then collected to measure residual PBDE concentrations. In addition, a control experiment was performed where no leaf powder was added to the PBDE solution.

The residual PBDE in the solution was analyzed using the method of Shih and Tai [33] with slight modifications. Briefly, 2 mL of a PBDE solution was added to bottles containing a mixture of acetone and *n*-hexane (1:1 *v/v*), and the bottles were shaken at 160 rpm for 2 h. The residual PBDE was extracted three times and then concentrated to 1 mL. PBDEs in the extracts were analyzed using the PerkinElmer Clarus 400 gas chromatograph (PerkinElmer, Waltham, MA, USA) equipped with

an electron capture detector. The carrier gas was nitrogen gas (chromatographic grade) and was injected at a flow rate of $3.5 \text{ mL} \cdot \text{min}^{-1}$ and a 20:1 split ratio. The sample injection volume was $1 \mu\text{L}$, with the temperature of the injector at 280°C and that of the detector at 300°C . The temperature of the initial column was set at 150°C for 5 min, increased at a rate of $5^\circ\text{C} \cdot \text{min}^{-1}$ to 280°C , and held for 15 min. The recovery percentages of BDE-3 and BDE-15 were 98.5% and 95.3%, respectively. The method detection limits of BDE-3 and BDE-15 were all $100 \mu\text{g} \cdot \text{L}^{-1}$.

2.5. Algal Biotoxicity Assays

Algal biotoxicity assays were performed using the freshwater unicellular green alga *C. vulgaris* Beij. #3001 because of its high sensitivity to contaminants. *C. vulgaris* was obtained from Prof. Wu of the Biodiversity Research Center (Academia Sinica, Taiwan). The algae were cultivated in the medium of Kuhl [34], and all cultures were maintained at 25°C under illumination of approximately $400 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ and a light-dark cycle of 14:10 h. To maintain log-growing cultures, the density of the cultures was maintained at 5–20 micrograms of chlorophyll *a* per liter by diluting them every two days.

The chlorophyll *a* content of *C. vulgaris* in BDE-3 or BDE-15 solutions before and after adsorption experiments was spectrophotometrically quantified at an absorbance of 680 and 750 nm, respectively. Before analysis, the low-cost adsorbents were removed through centrifugation at 8000 g for 5 min. The median effective concentration (EC_{50}) values for the inhibition of cell growth were evaluated to determine the PBDEs biotoxicity to the tested organism. The calculation of toxicity was based on the decrease rate of chlorophyll *a* content after the 24 h test period. The toxicity in a blank test without any PBDEs was also analyzed after the 24 h test period. The statistical calculation of these values was based on at least three repeated tests. Each test was performed using three replicate cultures.

2.6. Adsorption Rate Constants

The pseudo-second-order (PSO) model was applied to describe the adsorption rates of BDE-3 and BDE-15 by the leaf powder. The PSO model is a kinetic model proposed by Ho and McKay [35] based on the adsorption capacity. The adsorption of halogenated organic contaminants by leaf powders generally follows second-order kinetics with respect to the concentration of the parent contaminant. The mean value and standard deviation of the rate constant fit from three replicates are reported here. The equilibrium adsorption data was described by most frequently used Langmuir isotherm [36].

3. Results and Discussion

3.1. Characterization of Low-Cost Adsorbents

The physicochemical properties of the various adsorbents used in this study are shown in Table 1. The pH values of all the adsorbents ranged from 6.53 to 4.10. We observed that all adsorbents pretreated with one of the three pretreatment methods were weakly acidic. However, the pH value of the CT leaf powder pretreated with base washing was 8.12, indicating that CT leaf powder becomes alkaline during base washing. Zeta potential measurements revealed that the pH_{zpc} values of all adsorbents were lower than their pH values. Therefore, when the solution pH was greater than pH_{zpc} , the adsorbents exhibited a negatively charged surface and were favorable for adsorbing cationic materials.

The main constituents of the BT, GT, and CT leaves were cellulose, hemicelluloses, lignin, and pectin. The FTIR spectra of all leaf powder samples exhibited an intense and a broad band ranging from 3250 to 3550 cm^{-1} because of the hydrogen-bonded OH vibration of the cellulosic structure of the leaf powder. A strong and sharp band at 2922 cm^{-1} was attributed to the C-H stretching vibration from the CH_2 group of the cellulose and hemicelluloses. The peak at 1025 cm^{-1} was due to the C-O stretching of the carbonyl groups ($>\text{C}=\text{O}$) in the hemicelluloses. The bands at 1400 and 1648 cm^{-1} reflected C-N and C=C stretches, respectively. The FTIR spectra indicated that some surface functional

groups were present in the leaf powder samples. The SEM micrographs of different leaf powder samples at 1000 \times magnification are presented in Figure 1. These graphs revealed that the surfaces of the leaf powder samples were porous.

Table 1. Physicochemical properties of various adsorbents used in this study. Black tea (BT), Green Tea (GT), Coconut Palm (CT), acid washing (A-), base washing (B-), pressure steam washing (S-), pH at zero point of charge (pH_{zpc}).

Adsorbents	pH	pH _{zpc}	FTIR	Particle Size
BT	5.07	2.6	O-H, C-H, C-O, C=O, C=C, C-N	<0.149 mm
A-BT	4.86	2.6	O-H, C-H, C-O, C=O, C=C, C-N	<0.149 mm
B-BT	5.67	2.7	O-H, C-H, C-O, C=O, C=C, C-N	<0.149 mm
S-BT	5.07	2.8	O-H, C-H, C-O, C=O, C=C, C-N	<0.149 mm
GT	4.45	2.8	O-H, C-H, C=O, N-H, C-O	<0.149 mm
A-GT	4.10	2.1	O-H, C-H, C=O, N-H, C-O	<0.149 mm
B-GT	5.12	2.5	O-H, C-H, C=O, N-H, C-O	<0.149 mm
S-GT	4.58	2.6	O-H, C-H, C=O, N-H, C-O	<0.149 mm
CT	6.53	2.5	COOH, O-H, C=O, C-H, N-H, C=C	<0.149 mm
A-CT	6.07	2.0	COOH, O-H, C=O, C-H, N-H, C=C	<0.149 mm
B-CT	8.12	2.7	COOH, O-H, C=O, C-H, N-H, C=C	<0.149 mm
S-CT	6.40	2.5	COOH, O-H, C=O, C-H, N-H, C=C	<0.149 mm

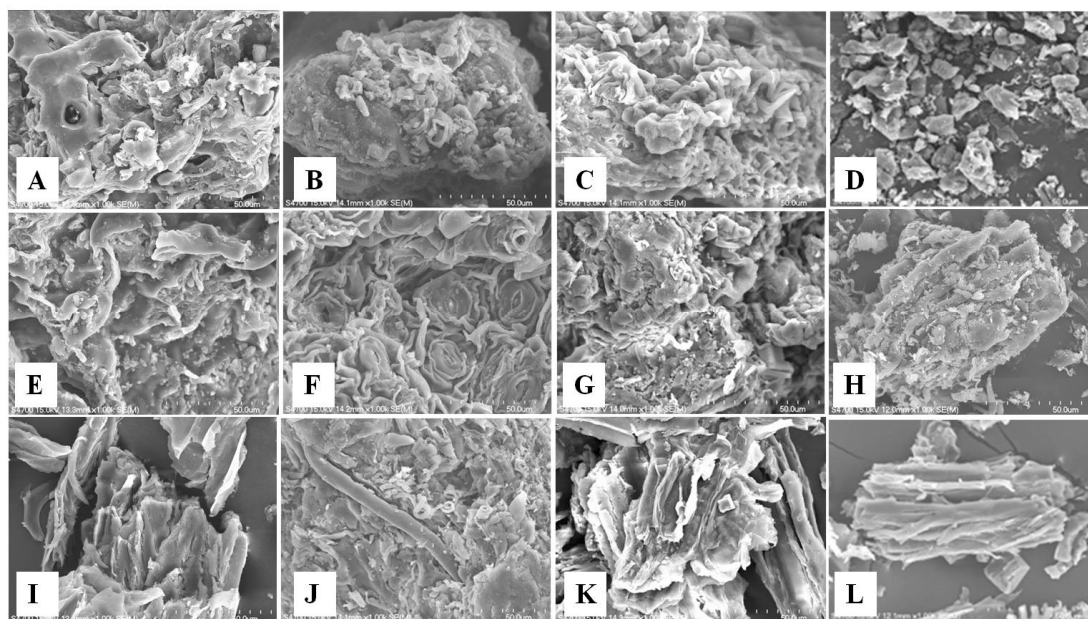


Figure 1. SEM images of leaf powder (1000 \times): (A) BT; (B) A-BT; (C) B-BT; (D) S-BT; (E) GT; (F) A-GT; (G) B-GT; (H) S-GT; (I) CT; (J) A-CT; (K) B-CT; and (L) S-CT. Black tea (BT), Green Tea (GT), Coconut Palm (CT), acid washing (A-), base washing (B-), pressure steam washing (S-).

3.2. Analysis of Adsorption Capacity

The pretreatment of adsorbents significantly affected their adsorption capacities. Figure 2 shows the adsorption capacities of different acid washing (A-) adsorbents for BDE-3 and BDE-15. The result showed that the adsorption of BDE-3 and BDE-15 increased with time. The A-BT adsorbent exhibited the highest adsorption capacity and the percentage of adsorption was 97.8%. The adsorption capacities of different base washing (B-) and pressure steam washing (S-) adsorbents are shown in Figures 3 and 4. The results showed that adsorbents pretreated with pressure steam washing (S-) exhibited the highest adsorption capacity. These results indicate that pretreating adsorbents with pressure steam washing could really affect and increase the adsorption capacity of adsorbents to adsorb BDE-3 and BDE-15.

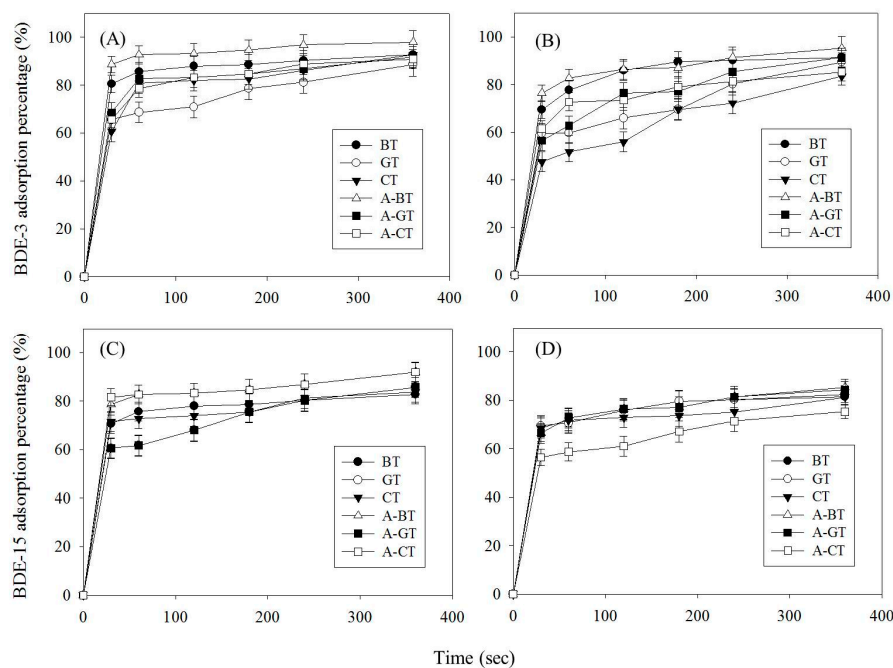


Figure 2. Adsorption capacity of different acid-washed (A-) adsorbents for BDE-3 (4-Dibromodiphenyl ether) and BDE-15 (4,4'-dibromodiphenyl ether): (A) $0.01 \text{ g}\cdot\text{L}^{-1}$ of different acid-washed adsorbents for BDE-3 adsorption; (B) $0.002 \text{ g}\cdot\text{L}^{-1}$ of different acid-washed adsorbents for BDE-3 adsorption; (C) $0.01 \text{ g}\cdot\text{L}^{-1}$ of different acid-washed adsorbents for BDE-15 adsorption; (D) $0.002 \text{ g}\cdot\text{L}^{-1}$ of different acid-washed adsorbents for BDE-15 adsorption.

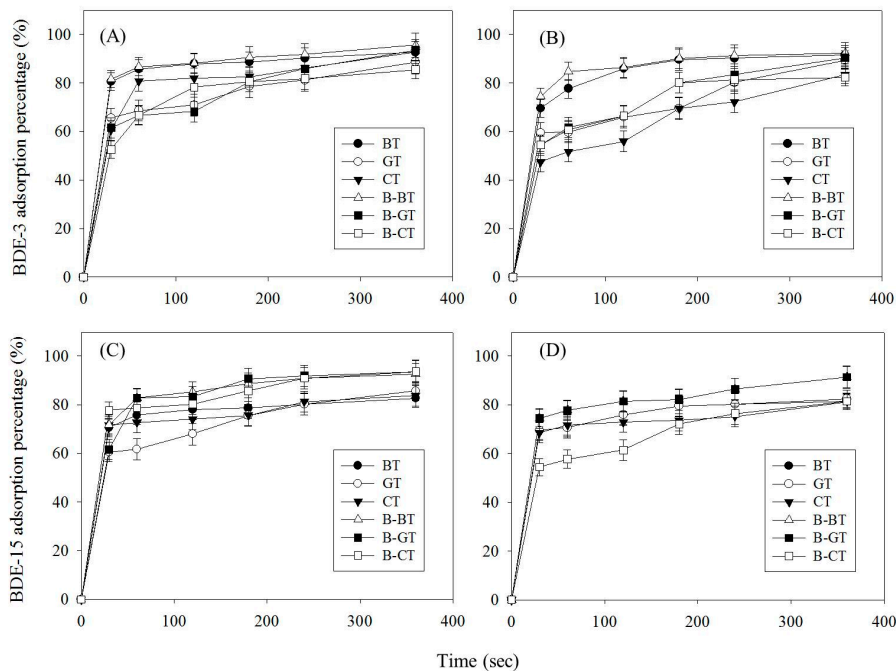


Figure 3. Adsorption capacity of different base washed (B-) adsorbents for BDE-3 and BDE-15: (A) $0.01 \text{ g}\cdot\text{L}^{-1}$ of different base-washed adsorbents for BDE-3 adsorption; (B) $0.002 \text{ g}\cdot\text{L}^{-1}$ of different base-washed adsorbents for BDE-3 adsorption; (C) $0.01 \text{ g}\cdot\text{L}^{-1}$ of different base-washed adsorbents for BDE-15 adsorption; (D) $0.002 \text{ g}\cdot\text{L}^{-1}$ of different base-washed adsorbents for BDE-15 adsorption.

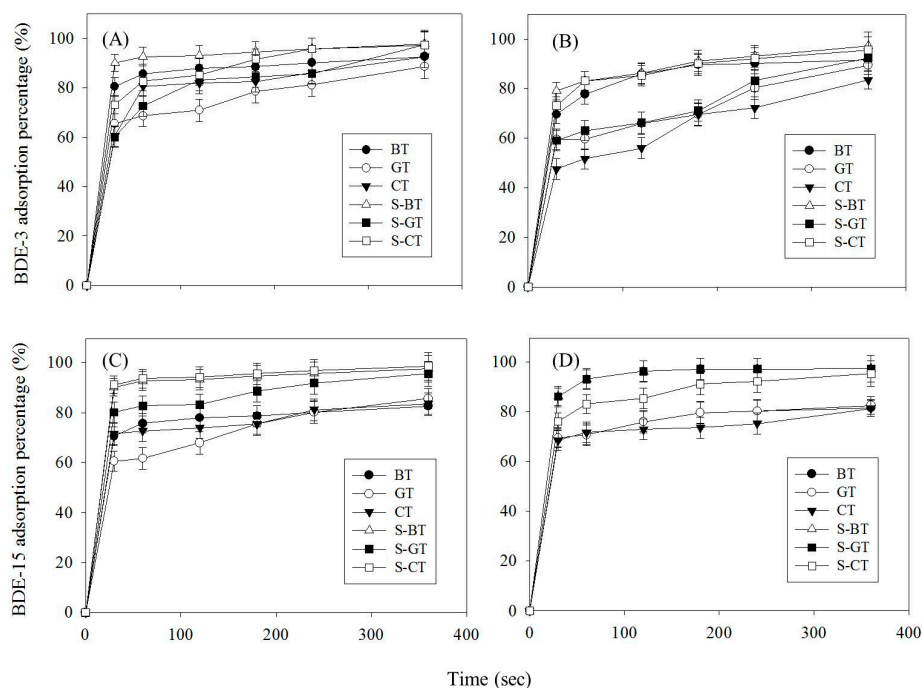


Figure 4. Adsorption capacity for BDE-3 and BDE-15 of different pressure steam-washed (S-) adsorbents: (A) $0.01 \text{ g}\cdot\text{L}^{-1}$ of different pressure steam-washed adsorbents for BDE-3 adsorption; (B) $0.002 \text{ g}\cdot\text{L}^{-1}$ of different pressure steam-washed adsorbents for BDE-3 adsorption; (C) $0.01 \text{ g}\cdot\text{L}^{-1}$ of different pressure steam-washed adsorbents for BDE-15 adsorption; and (D) $0.002 \text{ g}\cdot\text{L}^{-1}$ of different pressure steam-washed adsorbents for BDE-15 adsorption.

A comparison of different adsorbent doses for adsorbing BDE-3 and BDE-15 is presented in Table 2. The results showed that $0.01 \text{ g}\cdot\text{L}^{-1}$ of a BT adsorbent exhibited the higher adsorption capacities of BDE-3 and BDE-15 than did $0.002 \text{ g}\cdot\text{L}^{-1}$. The adsorption capacity of original BT was lower than other pretreated BT adsorbents, and the lowest BDE-3 and BDE-15 adsorption percentages of the original BT were 91.4% and 81.5%, respectively. The adsorption capacity of the BT adsorbent pretreated with pressure steam washing (S-BT) was higher than that of the other BT adsorbents, and its highest BDE-3 and BDE-15 adsorption percentages were 97.8% and 97.7%, respectively. Analyses of the adsorption capacities of the original GT and CT were also lower than other pretreated GT and CT adsorbents. The adsorption capacities of S-GT and S-CT were higher than those of the other GT and CT adsorbents. The highest BDE-3 and BDE-15 adsorption percentages of S-GT were 97.4% and 97.1%, respectively. The highest BDE-3 and BDE-15 adsorption percentages of S-CT were 97.3% and 98.5%, respectively. According to the best adsorption capacity results, 97.8% of BDE-3 and 98.5% of BDE-15 could be removed by pressure steam-washed adsorbents. The maximum adsorption capacities of S-BT, S-GT and S-CT, which were obtained from the Langmuir isotherms' fit, were $21.85 \text{ mg}\cdot\text{L}^{-1}$, $14.56 \text{ mg}\cdot\text{L}^{-1}$ and $22.47 \text{ mg}\cdot\text{L}^{-1}$, respectively. The maximum adsorption capacities of pressure steam-washed adsorbents were much higher than the Turkey tea waste ($8.64 \text{ mg}\cdot\text{L}^{-1}$) [37]. Differences in BDE-3 and BDE-15 adsorption capacities were due in part to the variation in properties from the origin of the low-cost adsorbents and the preparation of the adsorbents. The maximum adsorption capacities of S-BT, S-GT and S-CT were relatively high when compared with other low-cost adsorbents.

These results indicate that pressure steam washing might alter the surface of leaf powders and increase certain functional groups on their surface. Pressure steam washing may enable the diffusion of BDE-3 and BDE-15 ions from the solution to the surface of all adsorbents. Subsequently, the diffusion of molecules into the pores of the pressure steam-washed adsorbents occurs rapidly and easily. These findings can be used as the basis for applying these low-cost adsorbents for treating BDE-contaminated wastewater.

Table 2. Comparison of the effects of different adsorbent doses on BDE-3 (4-Dibromodiphenyl ether) and BDE-15 (4,4'-dibromodiphenyl ether) adsorption percentages (%).

	BDE-3		BDE-15	
	0.01 g·L ⁻¹	0.002 g·L ⁻¹	0.01 g·L ⁻¹	0.002 g·L ⁻¹
BT	92.7 ± 4.43	91.4 ± 4.02	82.6 ± 3.71	81.5 ± 3.36
GT	88.7 ± 4.57	89.4 ± 3.82	85.3 ± 4.03	82.4 ± 3.55
CT	92.7 ± 4.86	83.5 ± 3.55	83.1 ± 4.17	81.2 ± 3.27
A-BT	97.8 ± 4.95	95.2 ± 4.97	91.8 ± 3.79	85.3 ± 3.51
A-GT	91.9 ± 4.41	91.3 ± 4.12	85.6 ± 4.15	84.2 ± 3.46
A-CT	90.9 ± 4.03	85.3 ± 3.64	91.8 ± 4.14	75.3 ± 2.92
B-BT	95.5 ± 5.04	92.4 ± 4.26	92.5 ± 4.39	91.4 ± 4.51
B-GT	93.6 ± 4.38	90.4 ± 4.28	93.3 ± 4.45	91.6 ± 4.46
B-CT	85.6 ± 3.83	82.3 ± 3.52	93.5 ± 4.78	81.4 ± 2.95
S-BT	97.8 ± 5.53	97.3 ± 5.57	97.7 ± 5.34	97.2 ± 5.45
S-GT	97.4 ± 5.31	92.2 ± 4.82	95.6 ± 4.98	97.1 ± 5.35
S-CT	97.3 ± 5.45	95.5 ± 5.34	98.5 ± 5.56	95.3 ± 5.16

The given values are mean ± S.D. of three repeated tests.

The adsorption of BDE-3 and BDE-15 by all pressure steam-washed adsorbents was rapid and took only 4 min to reach the adsorption equilibrium (q_e). The adsorption shown in Figures 2–4 can be divided into three stages: (1) an initial stage with adsorption occurring instantly; (2) subsequent slow adsorption; and (3) a final stage with adsorption reaching the q_e and remaining constant. The first stage can be attributed to the rapid attachment of BDE-3 and BDE-15 to the surface of the adsorbents through surface mass transfer. At this stage, >75% of adsorption occurs in all adsorbents. The second stage was slower, possibly because many available external sites were already occupied and BDE-3 and BDE-15 molecules diffused slowly into the pore spaces of the adsorbent. An asymptotic trend was observed after approximately 2 min, regardless of the initial BDE-3 and BDE-15 concentrations applied to the adsorption system. The amount adsorbed did not vary significantly at contact times longer than the q_e time (4 min). The kinetics of the adsorption process indicated that the adsorption of BDE-3 and BDE-15 by all adsorbents pretreated with pressure steam washing was faster because >97% of BDE-3 and BDE-15 was adsorbed within 2 min. According to the results shown in Table 3, the k_2 of all pressure steam-washed adsorbents for BDE-3 adsorption ranged from 8.16×10^{-3} to $2.57 \times 10^{-2} \text{ g} \cdot (\text{mg} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$, and the amount adsorbed at q_e by all pressure steam-washed adsorbents for BDE-3 adsorption ranged from 4.43 to 4.72 $\text{mg} \cdot \text{L}^{-1}$. The k_2 of all pressure steam-washed adsorbents for BDE-15 adsorption ranged from 2.84×10^{-3} to $6.61 \times 10^{-2} \text{ g} \cdot (\text{mg} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$, and the amount adsorbed at q_e by all pressure steam-washed adsorbents for BDE-15 adsorption ranged from 4.21 to 4.78 $\text{mg} \cdot \text{L}^{-1}$. These results are consistent with those reported by Weng et al. [38]. The adsorption kinetics followed the PSO kinetic model, and intraparticle diffusion was involved in the adsorption process. These findings revealed the benefits of using these nonconventional, low-cost adsorbents for treating PBDE-rich wastewater.

Table 3. Pseudo-second-order adsorption rate constants and equilibrium values obtained with different pressure steam-washed adsorbents and PBDEs (Polybrominated diphenyl ethers).

	S-BT		S-GT		S-CT	
	BDE-3	BDE-15	BDE-3	BDE-15	BDE-3	BDE-15
Initial concentration ($\text{mg} \cdot \text{L}^{-1}$)	4.79	4.68	5.12	4.91	4.63	4.44
Weight of adsorbents ($\text{g} \cdot \text{L}^{-1}$)	0.002	0.002	0.002	0.002	0.002	0.002
q_e ($\text{mg} \cdot \text{L}^{-1}$)	4.66	4.55	4.72	4.78	4.43	4.21
k_2 ($\text{g} \cdot (\text{mg} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$)	2.57×10^{-2}	6.61×10^{-2}	8.16×10^{-3}	6.04×10^{-2}	2.52×10^{-2}	2.84×10^{-2}
r^2	0.993	0.998	0.941	0.998	0.997	0.996

3.3. Algal Biototoxicity of BDE-3 and BDE-15

The biototoxicity effects of BDE-3 and BDE-15 before and after adsorption experiments were examined using *C. vulgaris*. Both BDE-3 and BDE-15 exhibited high biototoxicity, and their EC₅₀ values were 7.24 and 3.88 mg·L⁻¹, respectively. Table 4 shows that the chlorophyll *a* content of *C. vulgaris* increased after adsorption, suggesting that after BDE-3 and BDE-15 were removed from the solution, their biotoxicities markedly decreased. The biotoxicities of adsorbents pretreated with pressure steam washing were lower than those in the blank. Compared with the blank, the chlorophyll *a* content of *C. vulgaris* in the BDE-3 solution after treatment with BT, GT, and CT adsorbents pretreated with pressure steam washing was 97.4%, 99.8%, and 99.6%, respectively, and that in the BDE-15 solution was 98.6%, 94.8%, and 97.5%, respectively. These results indicated that removing BDE-3 and BDE-15 through adsorption by adsorbents pretreated with pressure steam washing can significantly reduce the biototoxicity of BDE-3 and BDE-15 in the solution.

Table 4. Chlorophyll *a* content of *Chlorella vulgaris* (μg·kg⁻¹) before and after PBDE adsorption.

	Blank (without Any PBDEs) (μg·kg ⁻¹)	BDE-3		BDE-15	
		Before Adsorption (μg·kg ⁻¹)	After Adsorption (μg·kg ⁻¹)	Before Adsorption (μg·kg ⁻¹)	After Adsorption (μg·kg ⁻¹)
BT	1461 ± 24	1021 ± 14	1367 ± 16	696 ± 12	1343 ± 18
GT	1511 ± 28	786 ± 8	1401 ± 13	568 ± 8	1278 ± 11
CT	1507 ± 29	968 ± 12	1396 ± 14	556 ± 6	1253 ± 11
A-BT	1503 ± 29	985 ± 12	1387 ± 13	658 ± 8	1264 ± 15
A-GT	1488 ± 26	845 ± 12	1427 ± 15	548 ± 8	1254 ± 11
A-CT	1472 ± 23	845 ± 11	1354 ± 13	651 ± 7	1278 ± 13
B-BT	1531 ± 32	867 ± 11	1408 ± 14	632 ± 6	1298 ± 14
B-GT	1521 ± 31	931 ± 14	1432 ± 15	632 ± 6	1308 ± 12
B-CT	1481 ± 24	951 ± 11	1406 ± 14	598 ± 6	1346 ± 14
S-BT	1459 ± 25	976 ± 12	1421 ± 18	678 ± 11	1401 ± 21
S-GT	1473 ± 22	886 ± 11	1471 ± 21	641 ± 9	1394 ± 18
S-CT	1463 ± 24	1011 ± 13	1457 ± 16	617 ± 9	1421 ± 18

The given values are mean ± S.D. of three repeated tests.

4. Conclusions

The present study showed that the adsorption of BDE-3 and BDE-15 by various low-cost adsorbents was increased by pretreatment with pressure steam washing. The maximum adsorption capacities of pressure steam-washed black tea, green tea, and coconut palm leaf powders were 21.85 mg·L⁻¹, 14.56 mg·L⁻¹ and 22.47 mg·L⁻¹, respectively. In addition, 97.8% of BDE-3 and 98.5% of BDE-15 could be removed by pressure steam-washed adsorbents. Moreover, 0.01 g·L⁻¹ of the adsorbents exhibited higher adsorption capacities than 0.002 g·L⁻¹. An asymptotic trend was observed after approximately 2 min, regardless of the initial BDE-3 and BDE-15 concentration applied to the adsorption system. The amount adsorbed did not vary significantly at contact times longer than the *q_e* time (4 min). The adsorption kinetics followed the PSO kinetic model, and intraparticle diffusion was involved in the adsorption process. The highest S-BT adsorption constants (*k*₂) for BDE-3 and BDE-15 were 2.57 × 10⁻² and 6.61 × 10⁻² g·(mg·L⁻¹)⁻¹·s⁻¹, respectively. The EC₅₀ values of BDE-3 and BDE-15 in the algal biototoxicity assays were 7.24 and 3.88 mg·L⁻¹, respectively. After BDE-3 and BDE-15 were removed from the solution, their biototoxicity markedly decreased. Compared with various low-cost adsorbents, removing BDE-3 and BDE-15 through adsorption by adsorbents pretreated with pressure steam washing significantly reduced the biototoxicity of BDE-3 and BDE-15 in the solution. The results revealed that these low-cost adsorbents can be used for removing BDE-3 and BDE-15 from aqueous solutions.

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