Regeneration of Ion-Exchange Resins and Granular Activated Carbon with the Sonochemical Technique for Enabling Adsorption of Aqueous Per- and Polyfluoroalkyl Substances

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Abstract. Regeneration of adsorbents for reuse is crucial for reducing operating costs and maintaining sustainable systems. Few researchers have studied the regeneration of sorbents without using chemical solvents or appropriate methods. The purpose of this study was to evaluate the feasibility of the sonochemical technique (ST) for the regeneration of granular activated carbon (GAC), a mixed cation and anion resin (DOWEX MB-50), and an anion resin (IRA910) for the removal of per- and polyfluoroalkyl substances (PFAS). The ST was performed at 120 kW, and the power density was 250 W L⁻¹ for 30 min. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to examine physicochemical properties of the spent adsorbents. The removal efficiency of the spent adsorbent regeneration occurred in the following order: DOWEX > GAC > IRA910. As the PFAS-adsorbed adsorbents disappeared in the spectrum, the FTIR results showed the existence of a sulfonic group that is similar to the peaks of virgin sorbents. However, this method affected the morphology of GAC and IRA910 but not DOWEX MB-50. Consequently, the ST is a potential alternative to chemical regeneration for DOWEX MB-50 resins. It is also a potential method for an eco-friendly approach to regenerate PFAS-adsorbed materials.

1. Introduction
Per- and polyfluoroalkyl substances (PFAS) are a large group of manufactured compounds used in various products [1]. Perfluoroalkane sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) such as perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), which occur in source waters, are the dominant perfluoroalkyl acids (PFAAs) [2]. These substances can be transferred from the water to the ecosystem and then enter the food chain. Several studies have been published on the toxicology of PFAS in humans, which affects human health problems [3]. This is because of their ability to migrate, accumulate, and their inability to be eliminated with the conventional process [4]. Adsorption is one of the most promising approaches for treating PFAS from water [5]. In comparison with other technologies, adsorption presents advantages such as operational simplicity and low operating costs. Granular activated carbon (GAC) and ion exchange resins (IERs) are widely used in different separation processes [6]. The PFAS removal effectiveness was achieved on anion charge, cation charge, and both negative and positive charges [7].
Establishing the regeneration capability of spent sorbents is critical for increasing the use of adsorbents and economic competitiveness. Currently, research on regeneration has investigated thermal methods, solvent washing, and microwave regeneration [8]. Various factors influence the regeneration methods, including toxic substances, adsorbent types, and operating conditions. To date, few studies have investigated spent adsorbents without the use of chemical reagents on regeneration adsorbents. The sonochemical technique (ST) is superior with respect to the operating time, procedure, and temperature. The cavitation bubble with enormous energy was produced by a wavelength between 0.01 ~ 10 cm using ST [9]. Then, the adsorbents were separated from the sorbent surface and entered the bulk solution. The ST is environmentally friendly and it shows significant potential for PFAS removal [10]. Consequently, the ST is an interesting option for developing an effective method for renewing spent PFAS adsorbents.

This study investigates the regeneration efficiency of three types of adsorbents: granular activated carbon (GAC), an anion resin (IRA910), and a mixed cation and anion resin (DOWEX MB-50) using the ST based on the removal of PFOS and PFOA. Furthermore, the effect of the ST on the physicochemical structure of the adsorbents were explained by scanning electron microscopy (SEM) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR).

2. Materials and methods

2.1. Chemicals and adsorbents

2.1.1. Chemicals. Targeted per- and polyfluoroalkyl substances (PFAS), including perfluorooctanoic acid (PFOA, >95%) and perfluorooctane sulfonate (PFOS, 98%), were purchased from Wako Company in Japan. Methanol (MeOH, >99.99%) and acetonitrile (ACN, >99.8%) were purchased from Merck Company (Germany), both of which were of high-performance liquid chromatography (HPLC) grade. Ammonium acetate (NH₄CH₃CO₂, 99.9999%) was obtained from Fisher Chemical (USA). All solutions were prepared using Milli-Q water. Granular activated carbon (GAC), 1:1 by equivalents cation:anion resin (DOWEX MB-50), and a strong anion resin (Amberlite IRA 910 Cl) were purchased from Calgon Mitsubishi Chemical and Sigma Aldrich Company.

2.1.2. Preparation of adsorbents. GAC was washed with Milli-Q water at room temperature several times and boiled at 80 °C in Milli-Q water for 2 h to remove impurities. GAC was dried at 105 °C for 48 h and placed in a polypropylene (PP) tube. The resins were washed several times with Milli-Q water, followed by MeOH to remove impurities. Then, with the Milli-Q water wash was repeated to remove the remaining MeOH and dried at 40 °C for 48 h. Finally, the resins were stored in a desiccator.

2.2. Characterization of the adsorbents. The FEI Quanta 250 (FEI Ltd., Brno, Czech Republic) scanning electron microscope (SEM) was used to observe the surface morphologies of the saturated and regenerated adsorbents. The surface infrared spectra of the adsorbents were observed by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) using a Nicolet Summit Pro (Thermo Scientific, USA). Data acquisition with a transmittance scale was performed from 4,000 – 400 cm⁻¹ with a nominal resolution of 4 cm⁻¹.

2.3. Experimental design and regeneration procedure

2.3.1. Adsorption experiment. Sorbents (1 mg) were placed into PP bottles containing 100 mL of PFAS (PFOS and PFOA) solutions (1 mg L⁻¹). PFAS were prepared by dissolving in Milli-Q water. All samples were shaken at 120 rpm and 25 °C using an incubation shaker (n=2). The samples were analyzed for the remaining PFAS concentrations at different contact times (1, 3, 6, 12, 24, 48, 72, 96, and 120 h). Subsequently, the solution was passed through a 0.45 µm nylon membrane for analysis. The experiments were performed in duplicate. All the spent sorbents were collected for sonochemical regeneration.
2.3.2. **Sonochemical regeneration.** The spent adsorbents were added to 500 mL of Milli-Q water. Sonication step were carried out in a PP vessel reactor at frequencies of 130 kW and 20 kHz using a Cole-Parmer Ultrasonic Processor (USA). The applied power density was 250 W L\(^{-1}\) and the regeneration time was 30 min. Then, the spent adsorbents were washed with 500 mL of Milli-Q water to remove contaminants. Thereafter, the GAC and resins were dried at 40 °C for 48 h. The second adsorption experiment of PFASs was conducted by the spent adsorbent regeneration. Samples were collected at different times, as described in Section 2.3.1. Samples were then extracted using solid phase extraction (SPE) and analyzed using high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). Finally, the removal efficiency of spent adsorbent regeneration was calculated as shown in Equation (1):

\[
E \_i = \frac{E \_0}{E \_i} \times 100
\]

where \(E \_i\) = concentration of PFAS in the solution at contact time \(i\) (mg L\(^{-1}\))

\(E \_0\) = concentration of PFAS used in the adsorption experiment at time zero (mg L\(^{-1}\))

2.4 **Analytical methods for the detection of PFAS**

To investigate PFAS, the samples were analyzed using high-performance liquid chromatography (HPLC) with Agilent 1200 and Agilent 6410 triple quadrupole mass spectrometer (MS) (Agilent Technologies, USA). Each sample was prepared in duplicate. The column temperature was set at 40 °C. A mixture of ammonium acetate (NH\(_4\)CH\(_2\)CO\(_2\), 10 mM, A) (70 %) and pure acetonitrile (ACN, B) (30 %), with a flow rate of 0.25 mL min\(^{-1}\), was used as the mobile phase. This study used the HPLC-MS/MS method given in Sukseen et al. [11]. Furthermore, the calibration curves of at least five points were constructed over the concentration range of 2.5–50 µg L\(^{-1}\) for each analysis.

3. **Results and discussion**

3.1. **Performance for removal of PFAS with adsorbent regeneration.**

The adsorption capacity of perfluorooctane sulfonic acid (PFOS) (Figure 1(a)) exhibited a decrease from 30.99 mg g\(^{-1}\) in the virgin granular activated carbon (GAC) to 19.78 mg g\(^{-1}\) in the spent GAC regeneration. In the case of the anion resin (IRA910), the adsorption capacity was shown to decrease from 32.21 mg g\(^{-1}\) to 17.08 mg g\(^{-1}\). The results of the mixed cation and anion resin (DOWEX MB-50) was 29.33 mg g\(^{-1}\) for the virgin and 18.25 mg g\(^{-1}\) for the spent DOWEX MB-50 regeneration. Results of perfluorooctanoic acid (PFOA) using GAC (Figure 1(b)) adsorption capacity decreased from 30.55 mg g\(^{-1}\) to 19.65 mg g\(^{-1}\). IRA910 results decreased from 32.63 mg g\(^{-1}\) to 16.93 mg g\(^{-1}\). The adsorption capacity of DOWEX 50-MB decreased from 32.13 mg g\(^{-1}\) to 18.26 mg g\(^{-1}\). The results indicate that perfluoroalkane sulfonic acids (PFSAs) are more amenable than perfluoroalkyl carboxylic acids (PFCAs) due to the effects of the functional group [12]. Virgin DOWEX MB-50 has a higher adsorption capacity for PFOA than PFOS because of the concurrent hydrophobic interaction and the resin containing a hydroxyl group [13]. This is determined by comparing the removal efficiency of spent adsorbent regeneration calculated using equation (1). As observed, effective regeneration using the sonochemical technique (ST) would ensure more than 80% removal efficiency of the spent adsorbents. The removal efficiency of PFOA for spent IRA910 was the lowest when compared with that of GAC and DOWEX MB-50. The adsorption capacity of PFOA for spent IRA910 regenerated adsorbent diminished after regeneration. Therefore, the ST has a significant effect on the surface of IRA910 (Figure 2(f)), which influences the adsorption capacity. Compared with the surface area of GAC, the cracked surfaces did not influence the removal efficiency of the spent adsorbent regeneration.

However, a previously published study found that the carbon residues could be retained in pores and clogged the entrance of pores after the first cycle [14] and results in a reduction in the effective adsorption sites and adsorption capacity [15]. These results clearly indicate that DOWEX MB-50 is an efficient adsorbent with greater adsorptive capability and greater capacity for repeated use compared to
It may be possible that the influence of the DOWEX MB-50 properties was a mixture of cation and anion exchange resins. In addition, the surface of the resin was clean and smooth after regeneration (Figure 2(i)).

Figure 1. Comparison of (a) PFOS and (b) PFOA adsorption capacity on the different adsorbents.

Figure 2. Comparison of morphology of GAC, IRA910, and DOWEX: (a, d and g) virgin; (b, e and h) loaded with PFOS and PFOA; (c, f and i) after the sonochemical regeneration.

3.2. The surface morphologies of different types of adsorbents

To observe the effect of the sonochemical technique (ST), Figure 2(a) shows the surface of virgin GAC with diameters of approximately 400–600 µm. Virgin IRA910 and DOWEX MB-50 beads possessed intact, smooth, and spherical structures with diameters of 500–700 µm (Figure 2(d, g)). After PFAS were loaded onto IRA910 and DOWEX MB-50, the morphology was altered (Figure 2(e, h)). Moreover, small particles were observed on the GAC surface (Figure 2(b)). Overall, it was observed that the surface was clean, reconstituting the porosity of GAC and IRA910. After a regeneration time of 30 min, several cracks appeared on the GAC surface (Figure 2(c)). However, some adsorption sites were not fully restored, which may be associated with the accumulation of substances in the carbon during the application. Similarly, one study on regeneration revealed that carbon surfaces corroded to varying degrees [16]. After the ST, IRA910 (Figure 2(f)) showed that the erosion effect of cavitation was
significant on the surface. However, the surface of DOWEX MB-50 remained mostly intact (Figure 2(i)). Therefore, it was assumed that the ST could reduce regeneration efficiency as it can damage the GAC and IRA910 structures by inducing high-pressure shock waves and high-speed frequency.

Figure 3. ATR-FTIR spectrums of GAC (a), IRA910 (b), and DOWEX (c) at different stages.

3.3. ATR-FTIR analysis
As seen in Figure 3(a), GAC revealed distinct functional groups, including carboxyl (1398 cm⁻¹) and hydroxyl groups (3137 cm⁻¹). This is consistent with the understanding that GAC contains surface functional groups including carboxyls, lactones, carbonyls, phenolic hydroxyls, etc. [17]. After PFAS were adsorbed on GAC, the sulphur trioxide (SO₃) spectra (1088 cm⁻¹) were not observed in the spectrum of virgin GAC and regenerated GAC. The SO₃ spectra occurred on PFAS absorption (Figure 3(a)) because of the functional group of PFAS adsorbed on the GAC surface. The major bands of virgin DOWEX MB-50 (Figure 3(c)) showed characteristics of cross-linked styrene-divinylbenzene (styrene-DVB) in the 3000-3400 cm⁻¹ area, which have been detected in cation and anion resins [18].

The observed frequencies of the bands of virgin and spent DOWEX MB-50 are 3441 cm⁻¹, 2992 cm⁻¹, 2850 cm⁻¹, 1602 cm⁻¹, 1493 cm⁻¹, and 890 cm⁻¹ and represent –OH, C–H, –CH₂, C=C stretching vibrations, C=C (phenyl groups), and CH (p-disubstituted phenyl groups), respectively [19]. The evidence reported the absorbance of the cation (1008 cm⁻¹) and anion (890 cm⁻¹) [18]. Furthermore, the
peaks of PFOS/PFOA at 1148 cm$^{-1}$ were adsorbed onto the adsorbents [17], which is similar to the results of this study. Based on the FTIR spectra of IRA910 and DOWEX MB-50, after PFAS adsorption was observed at 1149 cm$^{-1}$ (Figure 3(b, c)), these were attributed to SO$_3$. The existence of SO$_3$ on the PFAS-adsorbed adsorbents disappeared in the spectrum, which was similar to the peaks of the virgin sorbents. Other researchers have reported that ST can degrade PFAS and improve the desorption rate of sorbents [10]. Therefore, the FTIR results implied that the ST achieved PFAS cleaning of spent sorbents.

4. Conclusion

Overall, these findings indicate that the use of the ST to generate adsorbents for PFAS adsorbed in water is an effective method for particular adsorbents. Under the condition that the frequency was 20 kHz, the applied power density was 250 W L$^{-1}$, and the regeneration time was 30 min, the removal efficiency of PFAS on spent adsorbent regeneration could reach 80% or more. Nevertheless, the ST in the reaction system affected the morphology of the as-treated GAC and IRA910. Hence, the use of the ST is appropriate for the regeneration of DOWEX MB-50. However, the use of ST for cleaning adsorbents should be investigated and measured against other techniques to ascertain the practicality of implementation.

Acknowledgment

This research was supported by the Doctoral Scholarship of Thailand Research Fund (PhD61I0022) for the Research and Researcher for Industry (RRI), Mahidol University, Thailand, and the On-site Laboratory Initiative from the Graduate School of Global Environmental Studies, Kyoto University, Japan.

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