

Article

Ion Exchange MIEX[®] GOLD Resin as a Promising Sorbent for the Removal of PFAS Compounds

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Abstract: Per- and polyfluoroalkyl substances (PFASs) are synthetic compounds, which have been widely produced, used, and recently identified as extremely toxic chemicals, and are responsible for serious environmental and human health risks. In this study, the removal efficiency of MIEX[®] GOLD resin was tested against six PFAS compounds including perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS), perfluorohexanoic acid (PFHxA), perfluorohexanesulfonic acid (PFHxS), perfluorooctanoic acid (PFOA), and perfluorooctanesulfonic acid (PFOS). The removal of PFASs and the regeneration of resin (NaCl-saturated methanol) were achieved via adsorption and desorption mechanisms. In all cases, the removal efficiency was greater than 99% where the volume ratio of 1 ppm PFAS to resin was maintained at 50-bed volume. Furthermore, the adsorption capacity of MIEX[®] GOLD resin was studied for PFOA and PFHxS and achieved 1.05 ± 0.01 g PFOA adsorption and 1.01 ± 0.04 g PFHxS adsorption per gram of resin. In addition, a detailed study on the interference of natural organic matter (NOM) and inorganic matter was carried out against PFHxA, PFOA, and PFOS. The presence of 10 ppm NOM (5 ppm tannic acid + 5 ppm humic acid) and 25 ppm inorganic matter (5 ppm nitrate + 20 ppm sulfate) showed no noticeable interference in the removal of selected PFAS compounds. Compared to sulfonic acid-containing PFASs, the interference of organic and inorganic matter on carboxylic acid-containing PFASs was slightly higher. The regeneration of PFAS-adsorbed resin was studied using a mixed solution containing 70% methanol and saturated NaCl. Desorption of PFHxS, PFOS, and PFOA was found to be 98.3, 100, and 43.3%, respectively. The results again indicate that the resin regeneration is strongly affected by the functional group of PFASs; i.e., resin with sulfonic acid-containing PFAS is much easier to regenerate than carboxylic acid-containing PFAS compounds. All the PFAS analyses were performed by using mass spectroscopy and liquid chromatography–mass spectroscopy. In conclusion, this study confirms the remarkable efficiency of MIEX[®] GOLD resin in removing PFAS compounds, even in the presence of a high concentration of organic and inorganic interferences, and its capacity to be regenerated for repeated usage. These advantages make MIEX[®] GOLD a promising product for the remediation of PFAS-contaminated water. This study in the broader sense proves that MIEX[®] GOLD is a promising adsorbent and provides the ground for future study to treat contaminated groundwater.

Keywords: PFAS compounds; MIEX[®] GOLD resin; removal efficiency; resin regeneration



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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are man-made, synthetic, organic, water-soluble chemicals, which have been widely manufactured and used over the last few decades. PFAS compounds exhibit high thermal, acid–base, and redox stability, are water and oil-repellent, and have unique amphiphilic properties. These advantageous properties lead to their extensive use both in industrial and household consumer products such as food packaging, non-stick cookware, cosmetics, waterproof and stain-proof textiles, carpet, furniture, mist suppressants, and fire-fighting foams [1–4]. The ubiquity of these chemicals

is revealed by data of their huge production in the United States since 1949, followed by worldwide production that is estimated to be in the tens of thousands of metric tonnes [5].

PFAS compounds contain a unique molecular structure that imparts excellent amphiphilic and physiochemical properties. The perfluoroalkyl moiety of the molecule confers hydro- and oleo-phobicity and thermal stability, and there is shielding of the carbon backbone from physical and chemical attacks due to the strong bonding of electronegative fluorine atoms, whereas the attached hydrophilic head group (a carboxyl or sulfonic group) imparts water solubility [1,6,7]. Such suitable physiochemical properties, chemical inertness, and resistance to degradation of PFAS compounds have caused their abundant global application leading to their global detection in widespread environment matrices such as aquatic, air, soil, wildlife, food, house dust, drinking water, groundwater, etc. [2–4,8–10]. Many of these synthetic chemicals can bioaccumulate in the food chain, can bind to blood lipoprotein, display proven toxicity in animal studies, and can cause potential harm to human health [2,11–13]. PFOS can accumulate in higher concentrations in different organs reporting high in liver (liver > muscle > kidney), whereas the opposite trend is identified for PFOA (muscle > kidney > liver) [12]. The environmental persistency, bioaccumulation, and potential health hazard aspects of PFASs have roused global attention and identified these substances as notorious environmental pollutants. Perfluorooctane sulfonic acid (PFOS) was included in the Stockholm Convention's Annex B as a global Persistent Organic Pollutant in 2009 because of its binding capability to plasma proteins and sequestration into the liver, kidney, and lungs [11,13]. Due to the potential toxic effects and public attention, the major US manufacturer 3M started phasing out and ceasing production of PFASs between 2000 and 2002, after 50 years of production [14]. In the years between 2000 and 2017, many countries including Australia, the USA, the UK, Canada, the Netherlands, Germany, Norway, and Sweden announced regulations and/or guidelines for the purpose of phasing out and limiting the use of PFAS compounds [15].

These studies have highlighted the necessity of the remediation of PFAS-contaminated sources such as groundwater, wastewater, soil, etc. One of the most popular and effective remediation strategies for PFAS is sorption. A wide range of adsorbents has been studied and some of the effective adsorbents include β -cyclodextrin polymer, activated carbon, fluorinated clays, anion-exchange resin, modified biomass, etc. [1]. Some of the commercial ion-exchange resins studied in PFAS removal include IRA67, IRA910, Amb IRA400, PFA300, PFA400, PFA444, A520E, A600E, A500p, A860, and A532E [1,7,16]. Scientific research shows various ion exchange resins (HPR4700, S6368, and A111S) as of high interest in PFAS removal by adsorption techniques [17]. There have also been a few reports on using magnetic ion exchange (MIEX) resin that was produced by Orica Watercare and IXOM Australia (MIEX[®] DOC resin) [18–20]. The MIEX[®] GOLD resin is a second-generation product of IXOM. Compared with MIEX[®] DOC, the advantageous features of MIEX[®] GOLD resin include increased surface area for greater adsorption capacity, larger porosity for easy access to the inner area and functional groups, and less steric or physical hindrance to enable the removal of both low (<5000 Da) and high molecular weight dissolved organic carbons [21]. It is expected that the new MIEX[®] GOLD resin would have better performance on PFAS removal.

In this study, we examine the removal efficiency of MIEX[®] GOLD resin for six selected PFASs, including perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS), perfluorohexanoic acid (PFHxA), perfluorohexanesulfonic acid (PFHxS), perfluorooctanoic acid (PFOA), and perfluorooctanesulfonic acid (PFOS). The interference of natural organic matter (NOM) (tannic acid and humic acid) and inorganic matter (sulfates and nitrates) on the removal capacity of PFAS compounds is then studied in detail. In addition, this study also explores the possible conditions (organic solvent and inorganic salt) to regenerate the PFAS-adsorbed resin. The regeneration study is important as it could reduce the PFAS remediation cost by reuse of the resin; it also provides insights into the understanding of the PFAS adsorption mechanism.

2. Materials and Methods

2.1. Materials

Perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS), perfluorohexanoic acid (PFHxA), perfluorohexanesulfonic acid (PFHxS), perfluorooctanoic acid (PFOA), and perfluorooctanesulfonic acid (PFOS) were purchased from Sigma-Aldrich (Pty. Ltd., Sydney, NSW, Australia). Methanol (MeOH), ethanol (EtOH), sodium hydroxide, sodium chloride, and ammonium chloride were purchased from Merck. Chromatography-grade acetonitrile, methanol, and formic acid were purchased from Sigma-Aldrich. MIEX[®] GOLD resin was obtained from IXOM Operations Pty Limited (Melbourne, Australia). Ultrapure water was obtained from a Millipore water purification system (Milli-Q) with a resistivity of 18.2 MΩ cm. All other reagents used were of analytical grade.

2.2. Pre-Treatment of MIEX[®] GOLD Resin

The MIEX[®] GOLD resin was washed to remove the impurities to avoid possible interference during analysis. Briefly, an amount of 5 mL resin was washed with 50 mL water by stirring at 180 rpm for 15 min. Then, this resin was collected using a rare earth magnet and transferred to 25 mL of 100% MeOH and kept mixing at 180 rpm for 15 min. This washing cycle was repeated three more times.

2.3. Removal of PFAS Compounds by MIEX[®] GOLD Resin

In all removal experiments, initial concentrations of PFAS compounds (PFBA, PFHxA, PFOA, PFBS, PFHxS, and PFOS) were maintained at 1 ppm. The volume ratio of PFAS to resin was kept consistent at 50-bed volume (BV). Briefly, 0.5 mL washed resin was mixed with 25 mL of 1 ppm PFAS solution. After stirring for 30 min at 180 rpm, the resin was removed carefully with a rare earth magnet. The unadsorbed PFAS in the solution was analyzed via mass spectroscopy (MS). Removal efficiency was calculated using the following equation:

$$\text{Removal efficiency (\%)} = 100 \times \left(\frac{\text{Initial amount of PFAS} - \text{PFAS remaining in Water}}{\text{Initial amount of PFAS}} \right) \quad (1)$$

2.4. PFAS Loading Capacity of MIEX[®] GOLD Resin

Capacity of the resin to remove or load PFHxS was performed by adding 0.5 mL resin (i.e., 0.11 g) to a PFHxS solution containing 0.1210 g PFHxS. This study was also performed at a 10 times larger scale by adding 5 mL resin to a solution containing 1.2306 g PFHxS. After overnight (12 h) adsorption with stirring at 180 rpm, the resin was removed and the solution was collected for PFHxS analysis using MS. Capacity of loading PFOA was performed following the same protocol where 0.5 mL resin was added to PFOA solution containing 0.1100 g PFOA.

2.5. Interference of Tannic Acid, Humic Acid, Sulfates, and Nitrates in PFAS Removal

Tannic acid (TA) and humic acid (HA) were selected to check the interference of natural organic matter (NOM) in the removal of six PFAS compounds (PFBA, PFBS, PFHxA, PFHxS, PFOA, and PFOS) by the MIEX[®] GOLD resin. In this regard, all experimental conditions were kept consistent as the PFAS removal (see Section 2.3) except for the presence of 1 ppm (0.5 ppm TA + 0.5 ppm HA) or 10 ppm (5 ppm HA + 5 ppm TA) NOM.

Interference of inorganic matter was checked following the same protocol where each PFAS concentration (PFHxS, PFOA, and PFOS) was kept at 1 ppm and the total concentration of inorganic matter was 25 ppm (5 ppm nitrate + 20 ppm sulfate).

Interference evaluation was also conducted with combined organic and inorganic matter at extremely high concentrations (50 ppm HA + 50 ppm TA + 250 ppm sulfate + 250 ppm nitrate). Each interference test was performed for each PFAS compound separately. All experiments were performed in duplicate and a collected sample aliquot was analyzed by using MS.

2.6. Regeneration of MIEX[®] GOLD Resin

Regeneration of PFAS-adsorbed MIEX[®] GOLD resin was initially studied for PFBA and PFOA-loaded resin to identify the most effective regenerant solution. Here, PFBA and PFOA-loaded resins were prepared following the protocol mentioned in Section 2.3 but the initial concentration of PFAS solution was 100 ppm. Then, the PFAS-adsorbed resin was collected carefully and used for the regeneration testing. One complete regeneration study takes a total of 4 h and ends up with BV 10. Four different regenerants were used, namely: (i) 60% MeOH with saturated NaCl, (ii) 60% MeOH with saturated NH₄Cl, (iii) 60% EtOH with saturated NaCl, and (iv) 60% MeOH with 0.0012% NaOH (pH 9.8). Briefly, 0.5 mL PFAS-adsorbed resin was added into 1.5 mL (3 BV) regenerant and mixed for 1 h at 180 rpm. Then, the resin was separated carefully, and this step was repeated two more times with fresh regenerant. Finally, 1 BV regenerant (0.5 mL) was added to the resin and mixed for 1 h. All regenerants were collected at the end of each cycle and combined (i.e., total 10 BV). The PFAS in the combined solution was measured. The regeneration efficiency of resin was calculated by quantifying the percentage of desorbed PFAS compound from resin with the following equation.

$$\text{Regeneration efficiency(\%)} = 100 \times \left(\frac{\text{Total PFAS adsorbed in resin} - \text{Total PFAS desorbed in regenerant}}{\text{Total PFAS adsorbed in resin}} \right) \quad (2)$$

Further regeneration studies were performed for three different PFAS-adsorbed resins, i.e., PFOA, PFOS, and PFHxS, using 70% MeOH with saturated NaCl, following exactly the same protocol as mentioned above, and LC-MS was used for quantitative analysis. Here, PFOA, PFOS, and PFHxS were loaded in resin following the same protocol mentioned in Section 2.3 (i.e., initial concentration of each PFAS was 1 ppm, and resin amount added was 0.5 mL). Regeneration of PFHxS was also conducted from supersaturated resin following the same regeneration protocol.

2.7. Material Characterization

Scanning electronic microscope (SEM) images were obtained on a field emission scanning electron microscope (FeSEM, ZEISS SUPRA 40VP, Oberkochen, Germany) at an acceleration voltage of 3 kV. The FTIR spectrum was obtained by using Thermo Scientific Nicolet iD5 spectrometer (Madison, WI, USA). The zeta potential value over pH range was obtained from Malvern Panalytical Zetasizer Pro/Ultra and MPT-3 Autotitrator. The UV–Vis absorbance spectra were measured with a UV–Vis spectrophotometer Shimadzu (Rydalmere, NSW, Australia). All MS and LC-MS analyses were performed by using Agilent 1290 Infinity II UHPLC with a 6545 Q-TOF MS (Agilent Headquarters, Santa Clara, CA, USA).

Direct injection method was used for the sample analysis to quantify the removal efficiency and loading capacity of PFAS into resin. Data acquisition and analysis were derived via Mass Hunter B.08.00 software. MS detection was carried out in negative ionization mode with the help of dual ESI and AJS (Agilent Jet Stream Technology) source (Agilent Headquarters, Santa Clara, CA, USA) ion source. The reference ion m/z values used for the detection of PFOA, PFOS, PFBA, PFBS, PFHxA, and PFHxS were 413.97, 499.93, 213.98, 299.95, 399.94, and 421.92, respectively. Other specifications include 0.3 mL/min flow rate, 4000 V capillary voltage, 350 °C sheath gas temperature, and 10.0 L/min and 20 psi nebulizer gas (nitrogen) flow rate and pressure, respectively. Sample injection volume was 5 µL. Solvent composition was 95% H₂O containing 0.1% formic acid and 5% acetonitrile. Samples were analyzed via LCMS to quantify the regeneration efficiency of MIEX-Gold resin where the separation was performed by using Agilent ZORBAX Eclipse Plus C18 column (USA) at 50 °C. Other specifications include 0.4 mL/min flow rate, 3500 V capillary voltage, 375 °C sheath gas temperature, and 8.0 L/min and 25 psi nebulizer gas (nitrogen) flow rate and pressure, respectively. A 95% H₂O containing 0.1% formic acid and 5% acetonitrile was selected as the mobile phase.

3. Results and Discussion

3.1. Characterization of MIEX[®] GOLD

In this study, MIEX[®] GOLD resin was used as an ion exchange resin to remove several PFAS compounds from water. The morphological and chemical properties of MIEX[®] GOLD resin were studied via SEM imaging, zeta potential measurement, and FTIR analysis.

Figure 1a,b represent SEM images of MIEX[®] GOLD resin at different magnifications. It can be seen that resin particles have irregular spherical shapes with rough surfaces. The particle size varies in a range of 100–250 μm , and this finding is in agreement with the supplied product detail, i.e., mean particle size of 180–250 μm .

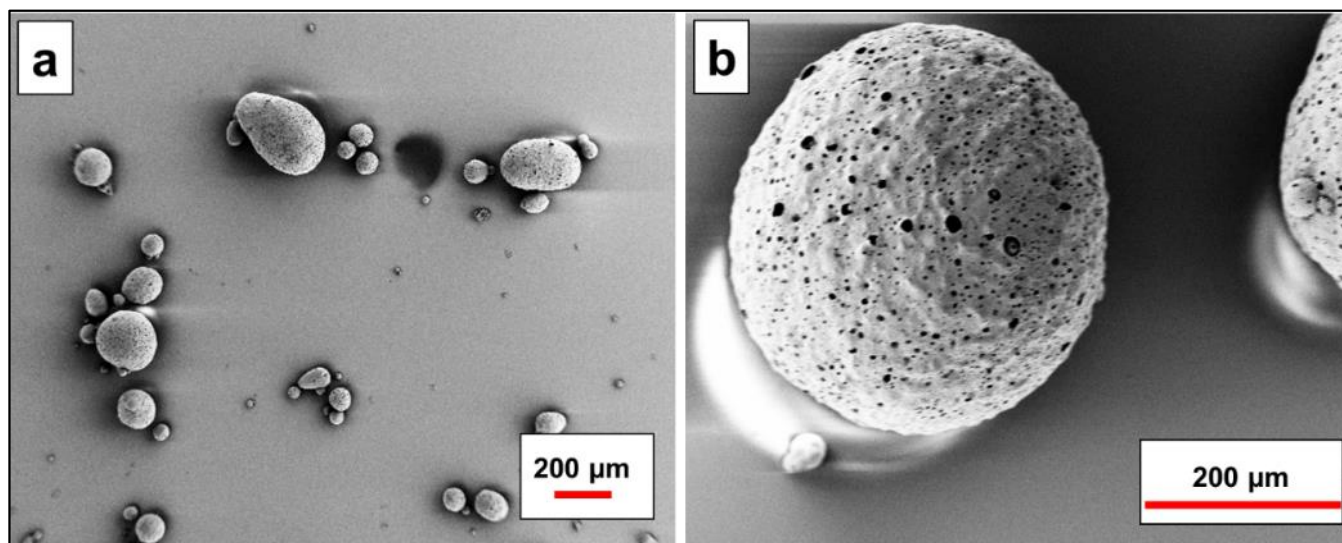


Figure 1. SEM images of MIEX[®] GOLD resin at (a) low and (b) high magnifications.

The zeta potential values of MIEX[®] GOLD resin over the pH range of 3–11 are presented in Figure 2a. The resins possess a positive surface charge over the whole pH range with decreasing surface charge above pH 6. This is attributed to the main functional groups of the resin being quaternary amines whose zeta potential value decreases with increasing pH.

MIEX[®] GOLD resin is a chemically macroporous methacrylic strong base anion exchange resin. Typically, magnetic ion exchange resin shows characteristic peaks of tertiary ammonium, alkyl, and $-\text{CH}_2$ groups [22–25]. The FTIR spectrum of MIEX[®] GOLD resin (Figure 2b) shows noticeable peaks at 1160 and 1720 cm^{-1} from the stretching of C–O and C=O groups [26]. Other characteristic peaks of the resin were noticeable at 1476 cm^{-1} from C–H symmetric bending (attached to the quaternary ammonium), 1387 cm^{-1} due to CH_3 symmetric bending, 1240 cm^{-1} from C–N stretching, and 967 cm^{-1} due to CH_2 rocking [22]. In addition, a characteristic peak at 1636 cm^{-1} was observed from the C=C skeleton vibration of the benzene ring [23,26].

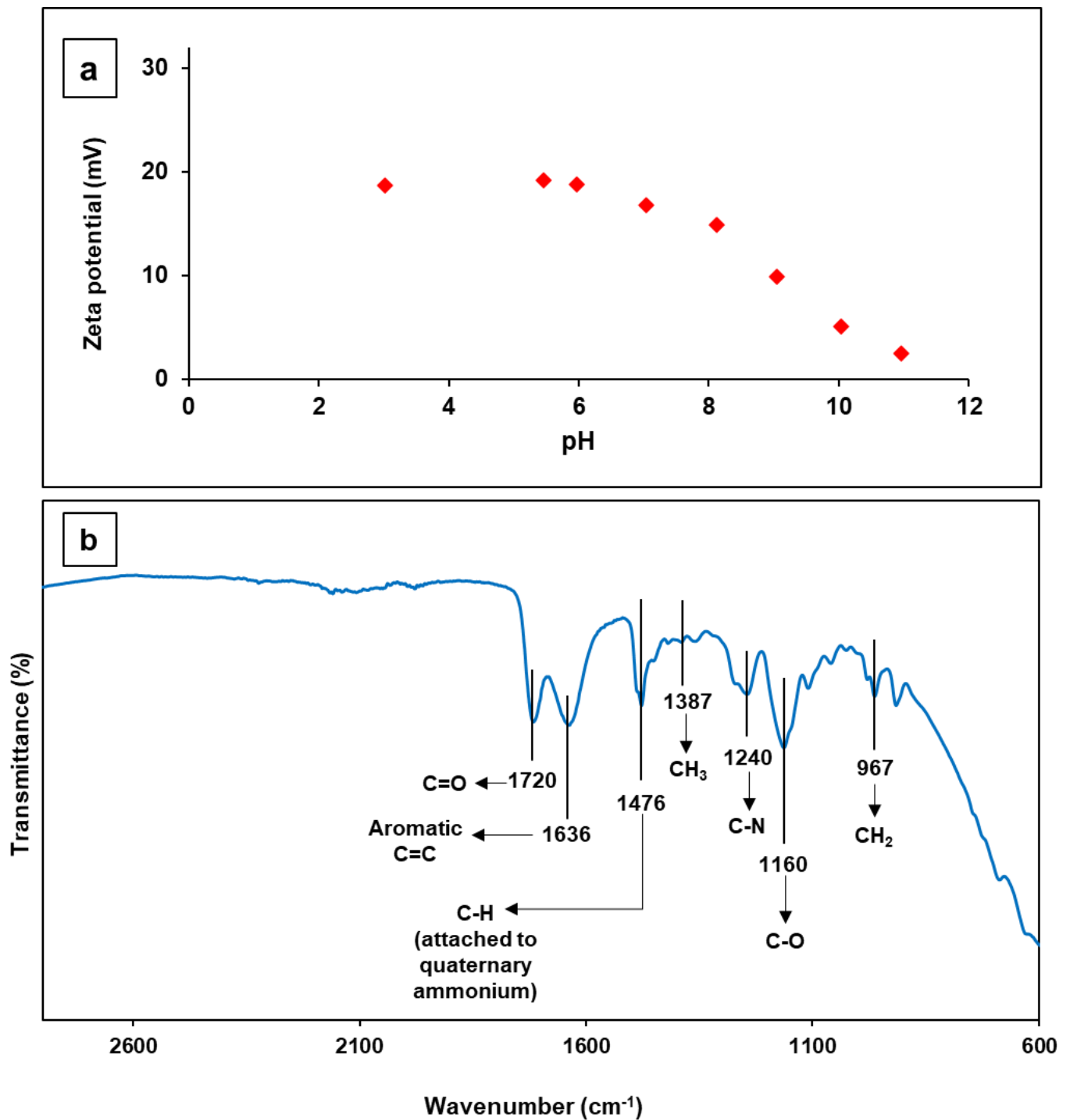


Figure 2. (a) The zeta potential (mV) for pH range 3–11, and (b) FTIR spectrum of MIEX[®] GOLD resin.

3.2. PFAS Removal Efficiency of MIEX[®] GOLD Resin

The removal efficiency of the resin was studied against six different PFAS compounds, which are PFBA, PFBS, PFHxA, PFHxS, PFOA, and PFOS. In all cases, the weight ratio of PFAS to resin was maintained at 1:4400 (i.e., 0.5 mL eq. to 0.11 g resin was used for 25 mL of each 1 ppm PFAS solution). Significantly, >99.999% removal of PFOA, PFOS, and PFHxS was estimated. On the other hand, $99.21 \pm 0.12\%$, $99.8 \pm 0.01\%$, and $99.65 \pm 0.00\%$ removal of PFBA, PFBS, and PFHxA, respectively, were quantified (Figure 3b).

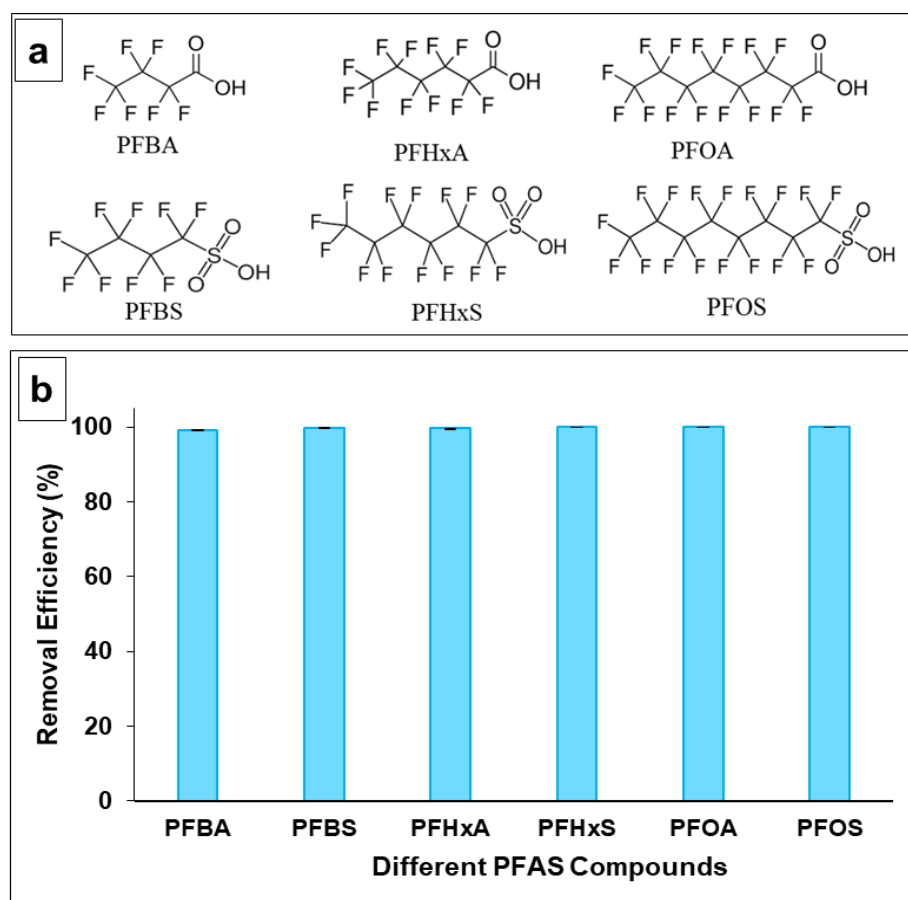


Figure 3. (a) Chemical structure of different PFAS compounds, and (b) Removal efficiency of MIEX® GOLD resin for PFBA, PFBS, PFHxA, PFHxS, PFOA, and PFOS.

Notably, the removal efficiency was found higher for longer-chain PFAS in comparison with shorter-chain PFAS. For example, PFOA (eight-carbon chain) showed more affinity for resin compared to shorter chain PFBA (four-carbon chain) and PFHxA (six-carbon chain). This was because the increased length of the alkyl group causes an increase in the hydrophobic character of PFAS compounds, which is more favorable to a passage from the solution to be adsorbed on resin. Regardless of smaller molecular size, PFBA and PFBS are less attracted or adsorbed to resin compared to longer chain homologs, which suggests no significant impact of size exclusion phenomena over the ion exchange phenomena of PFASs [7]. The results also showed that PFAS compounds with the sulfonic acid head group (e.g., PFHxS and PFBS) have slightly higher affinity to the resin compared to compounds with the carboxylic acid group (e.g., PFHxA and PFBA). Similar affinity was observed with other sorbents such as aminated sorbents, which exhibit higher affinity, efficiency, and selectivity toward sulfonic acid-containing PFASs [27]. This is mainly because the sulfonic acid head group of PFASs provides greater electrostatic interaction compared to the carboxylic acid head group toward the cationic quaternary ammonium group of adsorbents [8,27].

Figure 4 shows the schematic illustration of PFAS adsorption onto MIEX® GOLD resin. Negatively charged PFAS compounds in water can bind to the positively charged quaternary ammonium ion on the binding site of the resin surface by exchanging with the chloride ion. This ionic exchange caused the successful removal of PFAS compounds from contaminated water. This underlying mechanism of PFAS removal by MIEX® GOLD resin is similar to that of dissolved organic carbon removal by this resin [28]. The regeneration of resin is performed in MtOH (methanol) with saturated NaCl. The presence of a Na⁺ cation attracts the negatively charged PFAS from the positively charged quaternary ammonium

ion of resin beads. At the same time, an excess amount of chloride in the solution binds to the positively charged quaternary ammonium ion and helps to replace or desorb the adsorbed PFAS.

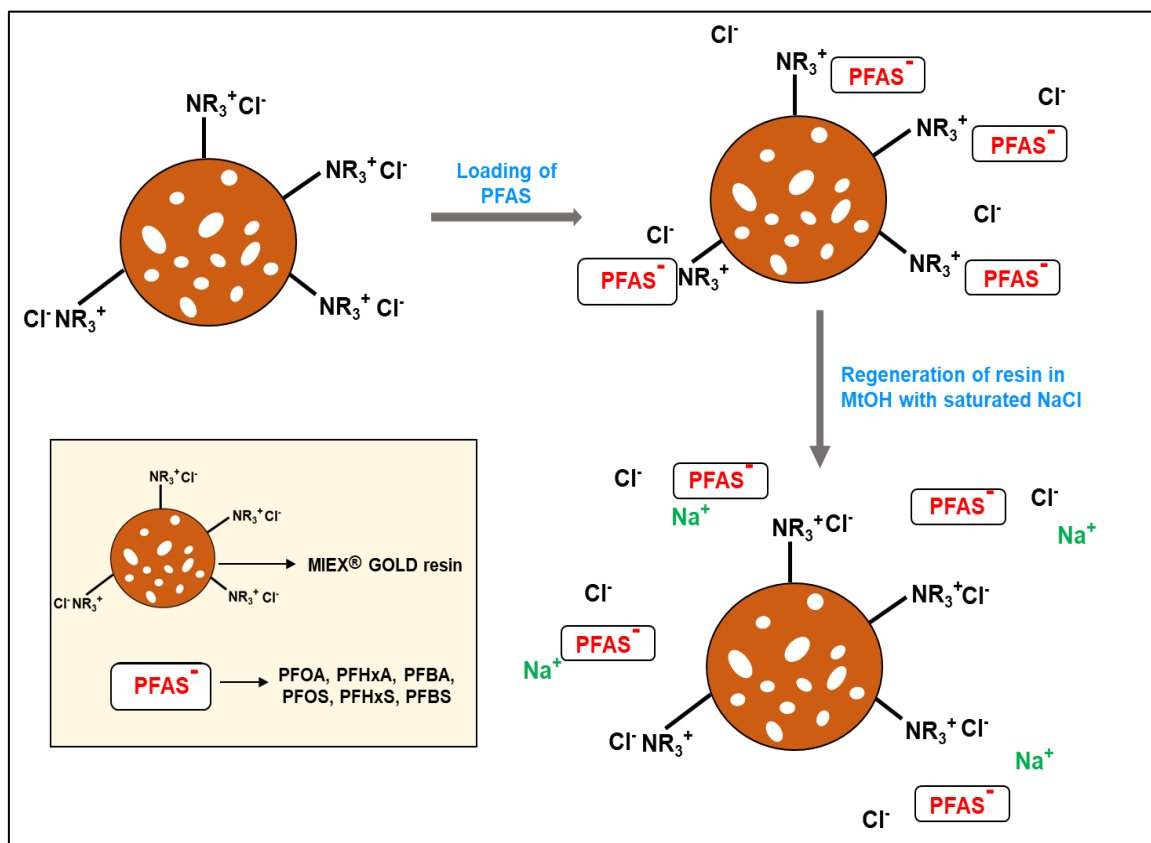


Figure 4. Schematic diagram of PFAS removal by resin and regeneration of PFAS-adsorbed MIEX® GOLD resin in MeOH with saturated NaCl.

The maximum adsorption capacity of MIEX® GOLD resin for PFOA and PFHxS was also determined. The result showed >90% adsorption capacity of MIEX® GOLD resin for both PFOA and PFHxS. The adsorption test for PFHxS was performed in two scales: (i) 0.11 g resin was exposed to 0.121 g PFHxS, and (ii) ten times larger scale by adding 1.1 g resin to 1.23 g PFHxS. Both scales showed similar results with an average of 1.01 ± 0.04 g PFHxS adsorption per gram of resin. This adsorption capacity for PFHxS (1.01 g/g) is significantly higher than other adsorbents, for example, magnetic activated carbon (0.13 g/g), few-layered porous graphite (0.612 g/g), and montmorillonite ($0.31\text{--}0.37 \times 10^{-3}$ g/g) [29,30].

The adsorption capacity of MIEX® GOLD resin for PFOA was also tested and 1.05 ± 0.01 g PFOA adsorbed per gram of resin was achieved. This value is much higher than the previously reported anion exchange resins such as PFA300 (0.117 g/g) [31], granular activated carbon (0.153 g/g), powered activated carbon (0.434 g/g), and anionic-exchange MIL101(Cr) metal–organic frameworks (0.49 and 0.78 g/g) [32,33]. Although this adsorption capacity is a little less than resin amberlite (IRA67, 1.16 g PFOA per gram), MIEX® GOLD resin requires comparably less time (12 vs. 48 h) to remove the same amount of PFOA [32].

3.3. Interference of Organic and Inorganic Matter on PFAS Removal

3.3.1. Interference of Organic Matter in PFAS Removal

Groundwater and wastewater commonly contain natural organic matter and organic pollutants that can compete with the removal of PFAS compounds leading to a decline in PFAS removal during the treatment of water [34–36]. One of the common organic

pollutants in water and wastewater is humic acid, which shows an important effect on PFOA adsorption [34]. In our study, two pollutants, namely, humic acid (HA) and tannic acid (TA), were selected to test the interference of NOM on the removal of PFAS compounds. In the absence of NOM, the removal of all studied PFAS was >99% (see above). Whereas in the presence of 1 ppm NOM, little influence was observed with >99.94% removal for all PFASs still achieved. Further study on the impact of NOM on PFAS removal was performed at higher concentrations of NOM when the concentration of the PFAS compounds was maintained at 1 ppm (Table 1). Even in the presence of 10 ppm NOM (i.e., 5 ppm HA acid + 5 ppm TA), high removal efficiencies of >99% were still achieved. Conclusively, there is negligible interference of NOM in the removal of PFAS compounds using MIEX[®] GOLD resin (Figure 5), even when the concentration of NOM is 10 times higher than PFAS.

Table 1. Removal efficiency of PFAS compounds with and without the interference of NOM and inorganic matter.

PFAS	Removal Efficiency (%) without Interference	Std ($\pm$)	Removal Efficiency (%) in 20 ppm Sulfate + 5 ppm Nitrate	Std ($\pm$)	Removal Efficiency (%) in 5 ppm Humic Acid + 5 ppm Tannic Acid	Std ($\pm$)	Removal Efficiency (%) in Inorganic and NOM at High Concentration *
PFHxS	100	0	99.88	0.09	99.82	0.02	91.00
PFOA	99.91	0.04	99.50	0.09	99.79	0.01	67.42
PFOS	100	0	98.40	1.00	99.94	0.90	94.35

* N.B. 50 ppm TA + 50 ppm HA + 250 ppm nitrate + 250 ppm sulfate.

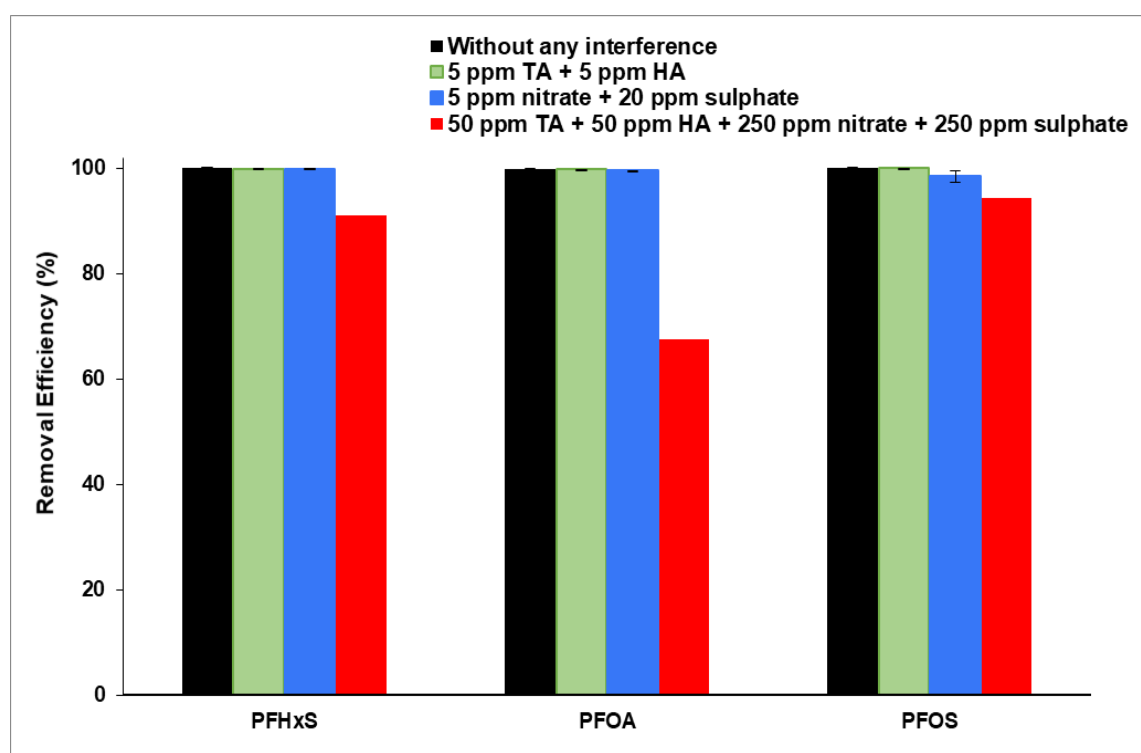


Figure 5. Interference of inorganic and organic matter on the removal of PFHxS, PFOA, and PFOS by MIEX[®] GOLD resin.

3.3.2. Interference of Inorganic Matter on PFAS Removal

Nitrate, sulfate, bicarbonate, and phosphate are common inorganic anions in groundwater. Two inorganic anions, namely, nitrate and sulfate, were selected to investigate the interference of inorganic matter on the removal of PFAS compounds by MIEX[®] GOLD resin. The influence of inorganic matter on PFAS adsorption was investigated by including 5 ppm nitrate and 20 ppm sulfate (total of 25 ppm inorganic matter) along with 1 ppm of each

PFAS compound (PFHxS, PFOA, and PFOS). The results indicated that for all three PFAS compounds, greater than 98% removal was achieved (Table 1). These results signified very little influence of inorganic matter on PFAS removal using MIEX[®] GOLD resin (Figure 5), even when the concentration is 25 times higher. Y. Gao and co-workers reported that the adsorption capacity of anion-exchange resin IRA67 for PFOS decreased 8.8% when the sulfate concentration was increased from 0 to 1.9 ppm (i.e., 2 mmol/L) [16]. Whereas, MIEX[®] GOLD resin showed no noticeable impact on PFOS adsorption when the sulfate concentration was increased from 0 to 20 ppm.

3.3.3. Interference of Highly Concentrated NOM and Inorganic Matter on PFAS Removal

The removal efficiency of PFHxS, PFOA, and PFOS was also studied in the presence of extremely high concentrations of both NOM (i.e., 50 ppm tannic acid + 50 ppm humic acid) and inorganic matter (i.e., 250 ppm nitrate + 250 ppm sulfate) to check any possible impact on PFAS adsorption for MIEX[®] GOLD resin. Notably, 67.42, 94.35, and 91.00% removal of PFOA, PFOS, and PFHxS were found, respectively, under these conditions with an extreme abundance of competitive pollutants (Figure 5, Table 1). Among these three PFAS compounds, PFOA showed a significant drop in removal efficiency from >99.9% removal to 67.4%. In contrast, both sulfonic acid head-containing PFAS compounds showed >90% removal efficiency. These data indicate that competitive ion influence on PFAS adsorption to resin is more prominent for carboxylic acid head-containing PFASs compared to sulfonic acid head-containing PFASs because sulfonated PFAS has a greater affinity toward the resin. A similar competitive interference of HA to PFOA adsorption on MIEX resin (a product of Orica Watercare) was found by Yang et al. [37]. They studied the removal efficiency of PFOA with increasing concentrations of HA from 0 to 4 ppm and observed a distinct decrease in the removal efficiency of PFOA from 93.9 to 74.0%. Such competitive interference results from the strong π - π interaction between HA and resin. Moreover, high concentrations of salts in solution can reduce the soluble PFAS compounds via the salt-out effect, which promotes the formation of PFAS micelles, eventually leading to the decline in PFAS removal by the resin [32].

3.4. Regeneration of MIEX[®] GOLD Resin

Previous research on resin recovery from PFAS adsorption showed that combined solutions of alcohols (e.g., methanol, ethanol) and inorganic salts (e.g., NH₄Cl, NaCl) were much more effective than using inorganic salts only, and the types and concentrations of alcohols and salts varied for different resins [7,17,32]. Based on these studies, three different regeneration conditions were selected to find out the most efficient regenerant for PFOA and PFBA saturated MIEX[®] GOLD resin. These regenerants were, namely, 60% MeOH with saturated NaCl, 60% MeOH with saturated NH₄Cl, and 60% EtOH with saturated NaCl.

The results indicated that 60% MeOH with saturated NaCl proved to be the best regenerant for the desorption of both PFBA and PFOA. An alkaline condition (60% MeOH with 0.001% NaOH) was also studied to evaluate the regenerating efficiency and was found completely ineffective. A similar ineffective observation with a 2% NaOH solution for regenerating strong anion resins (A600E, A520E, and A532E resins) was reported by A. Zaggia et al. [7]. Based on all results, MeOH with saturated NaCl could be considered the best regenerating solvent. We believe the mechanism of resin recovery is based on the dual effect of organic solvent MeOH and inorganic salt NaCl: while Cl⁻ is effective in desorbing the anionic hydrophilic head of the PFAS molecule from the ion exchange site of resin, MeOH assists in desorbing the hydrophobic carbon-fluorine tail from the resin backbone [38].

Further regeneration studies using 70% methanol with saturated NaCl to maximize PFAS desorption and regeneration efficiency were undertaken. The study was extended to include two sulfonic acid-containing PFAS (PFOS and PFHxS) to understand any effect from the PFAS chemical structure. Desorption of PFHxS and PFOS was found to be $98.3 \pm 0.5\%$ and 100%, respectively, whereas desorption of PFOA was only $43.3\% \pm 1.9$. Based on these

results, it is clear that the resin regeneration efficiency also depends on the type of PFAS compounds (i.e., functional group). The regeneration of sulfonic acid-containing PFAS (PFOS and PFHxS)-adsorbed resin is much higher than carboxylic acid-containing PFAS compounds (e.g., PFOA). As discussed earlier, the inorganic salt detaches the hydrophilic head of the PFAS molecule and MeOH desorbs the hydrophobic carbon-fluorine chain from the resin backbone. It seems that the chloride has a greater influence on the electrostatic interaction of the sulfonic acid head group compared to the carboxylic acid group of PFASs with the cationic quaternary ammonium group of resin, either through displacement or attraction of the PFAS. Moreover, MeOH plays a key role in desorbing the hydrophobic moiety, with the higher hydrophobicity of sulfonated PFASs compared to carboxylic acid PFASs being another reason, resulting in higher regeneration efficiency of sulfonic acid-containing PFAS (PFOS and PFHxS)-adsorbed resin compared to carboxylic acid-containing PFAS compounds.

4. Conclusions

In summary, we have successfully achieved satisfactory removal efficiency for six selected PFASs (PFBA, PFBS, PFHxA, PFHxS, PFOA, and PFOS) using MIEX[®] GOLD resin. In general, the removal efficiency was found to be >99% for the selected PFAS. Briefly, significant removal (>99.999%) of PFOA, PFOS, and PFHxS was obtained. Whereas, $99.21 \pm 0.12\%$, $99.8 \pm 0.01\%$, and $99.65 \pm 0.00\%$ removal of PFBA, PFBS, and PFHxA, respectively, was estimated. The maximum adsorption capacity for PFHxS (1.01 ± 0.04 g/g resin) and PFOA (1.05 ± 0.01 g/g resin) is noteworthy. In addition to these outcomes, a comprehensive study on the interference of organic and inorganic matter showed a very negligible impact on PFAS removal with >99% removal of selected PFAS compounds at low concentrations of both inorganic matter and NOM. However, a high concentration of NOM and inorganic matter showed an influence on the removal of PFOA (67.42%), but significant removal (>90%) of PFOS and PFHxS was still achievable. Moreover, >98% regeneration efficiency of PFOS and PFHxS-adsorbed resin in 70% methanol with saturated salt was achieved, which will significantly reduce the remediation cost through the reuse of the resin. Overall, MIEX[®] GOLD resin has been found to be very promising as an efficient and cost-effective sorbent for the treatment of PFAS-contaminated water.

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