Supplementary Information

Efficient removal of short- and long-chain perfluoroalkyl carboxylate acids from surface water matrices using quaternary ammonium functionalized adsorbent derived from waste Karanja shells

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S1. Synthesis of adsorbent

In this study, a waste-derived adsorbent was synthesized from Karanja *(Pongamia pinnata)* shells through a controlled activation and surface functionalization process. The raw Karanja shells were collected from the IIT Bombay campus and initially dried in a hot air oven at 80°C. Once dried, the shells were ground through grinder and subsequently sieved to obtain a powder suitable for synthesis of adsorbent. The synthesis of activated carbon (AC) was achieved through a single-step chemical activation method, by using ortho-phosphoric acid (H_3PO_4) as the activating agent. The activation process involved impregnating the powdered biomass with H_3PO_4, followed by carbonization at an optimized temperature of 450°C under a limited oxygen environment. The obtained AC was thoroughly washed with NaOH solution followed by DI water to neutralize any residual acidic components. A surface modification using cetyltrimethylammonium bromide (CTAB) was performed to functionalized AC with quaternary ammonium functional groups. The functionalized AC was subsequently washed to remove unreacted reagents, stabilized, and stored for further experimental uses.

Table S1. Salient properties of TP-108 ion-exchange resin (LEWATIT® TP 108)

Characteristics	Description
Matrix	Styrenic
Functional groups	Quaternary ammonium
Physical form	Spherical Beads
Total exchange capacity	$\geqslant$0.7 eq/L
Moisture holding capacity	33–43%
Effective size	0.460–0.610 mm
Uniformity coefficient	$\leqslant$1.7

Table S2. Salient properties of Purofine™ PFA694 ion-exchange resin (Purolite™)

Characteristics	Description
Matrix	Polystyrene crosslinked with divinylbenzene
Functional groups	Complex Amino
Physical form	Spherical Beads
Specific Gravity	1.3
Effective size	0.675±0.0750 mm
Uniformity coefficient	⩽1.3

S2. Experimental protocol for batch studies

Batch adsorption studies were conducted to determine the equilibrium adsorption capacity of the adsorbent for each PFCA compound. The initial PFCA concentrations ranged from 0.1 to 10 mg/L, while the adsorbent dose was maintained at 15 mg per 100 mL of solution. To assess the adsorbent's performance in the presence of multiple PFCAs, batch experiments were conducted using a mixture of all four PFCA compounds at concentrations ranging from 0.1 to 1 mg/L, under the same adsorbent dose and solution volume conditions. For isotherm study, initial and final concentration of PFCAs were measured after batch process and equilibrium uptake capacity of adsorbent (Q_e) was calculated using the equation S1. Different existing isotherm models were checked for modelling of experimental data (Q_e vs C_e plot). Among all, Langmuir (eqn. S2) and Toth (eqn. S3) isotherm model exhibited good fitting with experimental data. Experimental data of rate kinetic study was fitted with the pseudo first (eqn. S4) and second order (eqn. S5) rate kinetic models.

$$Q_e = \frac{(C_i - C_e) * V}{m} \qquad \text{(S1)}$$

$$Q_e = \frac{Q_L * C_e * b}{1 + bC_e} \qquad \text{(S2)}$$

$$Q_e = \frac{(Q_T * C_e * K_t)}{\{1 + (C_e * K_t)^{M_t}\}^{1/M_t}} \qquad \text{(S3)}$$

$$Q_t = Q_e(1 - e^{-K_1 * t}) \tag{S4}$$

$$Q_t = \frac{(K_2 * Q_e^2 * t)}{(1 + Q_e * t * K_2)} \tag{S5}$$

where, C_e and C_i are equilibrium and initial concentration of adsorbate, Q_e= Equilibrium adsorption capacity of adsorbent (mg/g), Q_L= Langmuir maximum adsorption capacity (mg/g), b= Langmuir constant (L/mg), Q_T= Toth maximum adsorption capacity (mg/g), M_t= Toth heterogeneity factor and K_T= Toth constant (L/mg). K_1 (min^{-1}) and K_2 ($g*mg^{-1}*min.^{-1}$) are rate constant of pseudo first and second order models, respectively.

S3. Selectivity Study

Impact and interference caused by presence of background species was evaluated through the measure of percent removal (eqn. S6) of PFCA. An initial concentration of 100 μg/L was prepared for each PFCA, resulting in a total ∑PFCA concentration of 400 μg/L for experiments. The experiments were conducted in the presence of individual background species to evaluate their influence on PFCA adsorption. A volume of 100 mL was used for each reaction, and 15 mg of the adsorbent was added. The pH of the solutions was adjusted and maintained at 7 for all the experiments. The concentrations of these background species were taken from a river water matrix [1] and values were as follows in milli equivalents per litres (meq/l) : carbonate (CO_3^{2-}): 2.25 meq/l, sulphate (SO_4^{2-}): 0.5 meq/l, phosphate (PO_4^{3-}): 0.5 meq/l, silicate (SiO_3^{2-}): 0.5 meq/l, calcium (Ca^{2+}): 1.5 meq/l, and magnesium (Mg^{2+}): 0.5 meq/l.

$$Removal\ percent = \frac{(C_i - C_e)}{C_e} * 100\% \tag{S6}$$

S4. Packed-bed column study

Continuous-flow experiments were conducted using a packed-bed column setup, as shown in Figure S1. A fixed quantity of the synthesized adsorbent (1.550±0.01 g) was introduced into the column as a slurry, and stable operating conditions were established. The flow rate was controlled using a peristaltic pump (Masterflex® L/S) equipped with silicone tubing (L/S-16). The packed-bed column used in this study had an internal diameter (D) of 1.1 cm and a packed-bed height (Z) of 6.3 cm. Scale-up of the column was guided by established design criteria to ensure effective bed utilization and minimize axial dispersion. Specifically, the column dimensions were selected to satisfy the conditions $Z/D \geq 5$ and $D/d_p \geq 12–30$, where d_p represents the mean particle diameter of the adsorbent[2]. The compositions of the inlet water matrices of river and lake water, are detailed in Tables S3 and S4, respectively. Effluent samples were collected at regular intervals, and PFCA concentrations were analysed.

Figure S1: Packed-bed column setup for continuous flow study.

Table S3: Composition of the Ganga water matrix [1] used in the study:

Name of species	Concentration (mg/L)
Ca^{2+}	32±2.5
Mg^{2+}	22±2.5
Cl^-	27±2.5
NO_3^-	0.5±0.1
PO_4^{3-}	15±2.5
SiO_3^{2-}	20±2.5
$HCO3^-$	165±5
SO_4^{2-}	25±2.5
PFOA (spiked)	0.1
pH	8.3±0.5

Table S4: Composition of the lake water matrix [3] used in the study:

Name of species	Concentration (mg/L)
Ca^{2+}	147±5
Mg^{2+}	32±2.5
Cl^-	305±5
NO_3^-	27±2.5
PO_4^{3-}	31±2.5
SiO_3^{2-}	17±2.5
$HCO3^-$	792±5
SO_4^{2-}	74±2.5
PFOA (spiked)	0.1
pH	8±0.5

S5. Details of Analytical techniques

Method of UHPLC was developed through optimization of LC and MS parameters. Mass spectrometry (MS) conditions were optimized by injection of standards of four compounds individually. Values of precursor and product ions for MS analysis are shown in Table S5. Gradient of mobile phase (eluent) of LC for chromatographic separation is shown in Table S6.

Global parameters for MS were as follow:

Ion source type- H-ESI, Spray Voltage- Static, Positive Ion (eV)- 3500, Negative Ion (eV)- 2500, Sheath Gas (Arb)- 50, Auxiliary Gas- 1, Ion transfer Tube Temperature (C)- 325, Vaporizer Temperature (C)- 350.

Solid Phase Extraction (SPE): SPE was employed to remove background ions from the simulated river and lake water samples prior to LC-MS analysis. Oasis WAX cartridges (60 µm, 6 cc, 500 mg), obtained from Waters Corporation, were utilized for the extraction of PFCAs. The cartridges were preconditioned before passing the water samples through them. Elution of PFCAs was performed using methanol, followed by 0.5% (v/v) ammonium hydroxide in methanol. The obtained extracts were subsequently filtered and analysed for PFCA using LC-MS.

Table S5: Values of precursor and product ions for MS analysis

Compound Name	Precursor ion (m/z)	Product ion (m/z)	RF Lens (V)	Collision Energy (V)
PFPrA	162.9824	119.018	42	10.05
PFBA	212.9792	168.625	60	9.3
PFPeA	262.976	218.99	63	8.66
PFOA	412.878	169, 218.878, 368.958	116, 116, 116	18.23, 15.99, 9.68

Table S6: Flow graidient of LC mobile phase

No.	Time (min.)	Flow (ml/min.)	% Organic	% Aqueous
1	0.0	0.25	2	98
2	0.5	0.25	10	90
3	1.5	0.25	30	70
4	4.6	0.25	80	20
5	4.7	0.25	95	5
6	7.4	0.25	95	5
7	7.5	0.25	10	90
8	11.9	0.25	2	98
9	12.0	0.0	2	98

S6. Results

Table S7: Values of isotherm model parameters for batch experiments performed with PFCA individually

	PFOA (C8)	**PFPeA (C5)**	**PFBA (C4)**	**PFPrA (C3)**
Langmuir Model				
Qm (mg/g)	34.962	29.221	19.627	15.025
b	0.0026	0.0022	0.0018	0.0012
RSQ	0.914	0.917	0.945	0.960
Toth Model				
Qt (mg/g)	36.473	29.087	20.321	17.115
Kt	0.002	0.002	0.006	0.0029
Mt	1.259	0.943	0.578	0.514
RSQ	0.950	0.936	0.958	0.972

The mathematical expressions of the Langmuir isotherm model to describe the adsorption capacity (Q_e) of PFCAs under equilibrium conditions are as below:

$$Q_e = \frac{C_e * 0.091}{1 + 0.0026 * C_e}$$

(S7)

$$Q_e = \frac{C_e * 0.0643}{1 + .0022 * C_e}$$

(S8)

$$Q_e = \frac{C_e * 0.0353}{1 + .0018 * C_e}$$

(S9)

$$Q_e = \frac{C_e * .018}{1 + .0012 * C_e}$$

(S10)

Table S8: Values of isotherm model parameters for batch experiments performed with PFCA mixture

	PFOA (C8)	**PFPeA (C5)**	**PFBA (C4)**	**PFPrA (C3)**
Langmuir Model				
Qm (mg/g)	**10.430**	**8.607**	**6.04**	**3.987**
b	0.160	0.120	0.021	0.012
RSQ	0.945	0.932	0.980	0.957
Toth Model				
Qt (mg/g)	9.487	8.564	5.970	4.102
Kt	0.112	0.071	0.021	0.008
Mt	1.611	1.694	1.859	1.4
RSQ	0.985	0.941	0.975	0.986

Table S9: Values of rate kinetic model parameters

	PFOA (C7)	**PFPeA (C5)**	**PFBA (C4)**	**PFPrA (C3)**
Pseudo Second Order Model				
Qe (mg/g)	35.787	26.033	18.901	12.766
K_2 (g*mg$^-$	0.001	0.003	0.007	0.018

^{1}*min.$^{-1}$)				
RSQ	0.97	0.95	0.96	0.92
Pseudo First Order Model				
Qe (mg/g)	33.431	24.095	16.464	11.322
K_1 (min.$^{-1}$)	0.035	0.054	0.1	0.128
RSQ	0.934	0.92	0.95	0.89

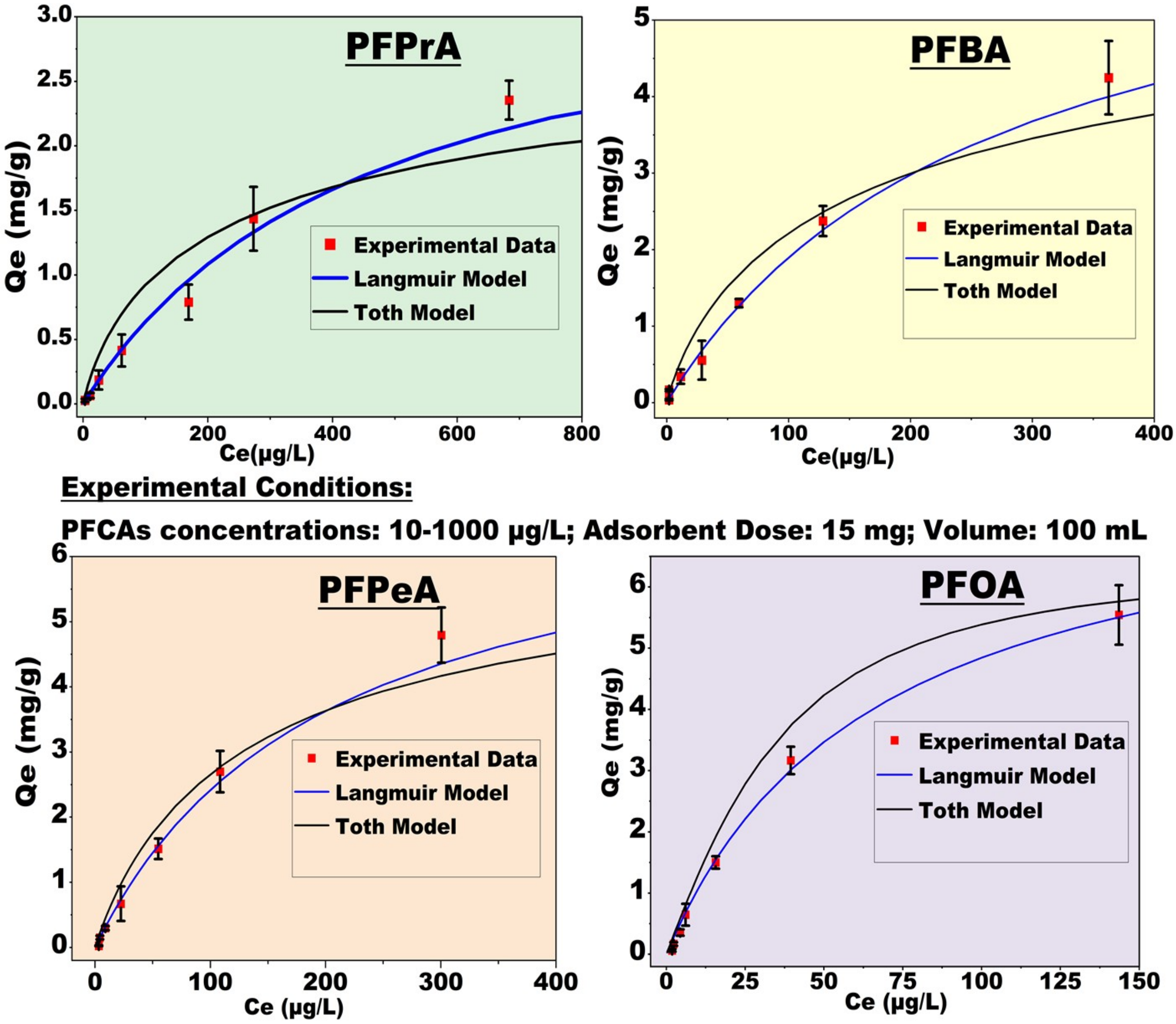


Figure S2: Isotherm model plots of PFCAs adsorption (Initial PFCA conc. 0.01 to 1 mg/L, Adsorbent dose:15 mg, Volume: 100 mL)

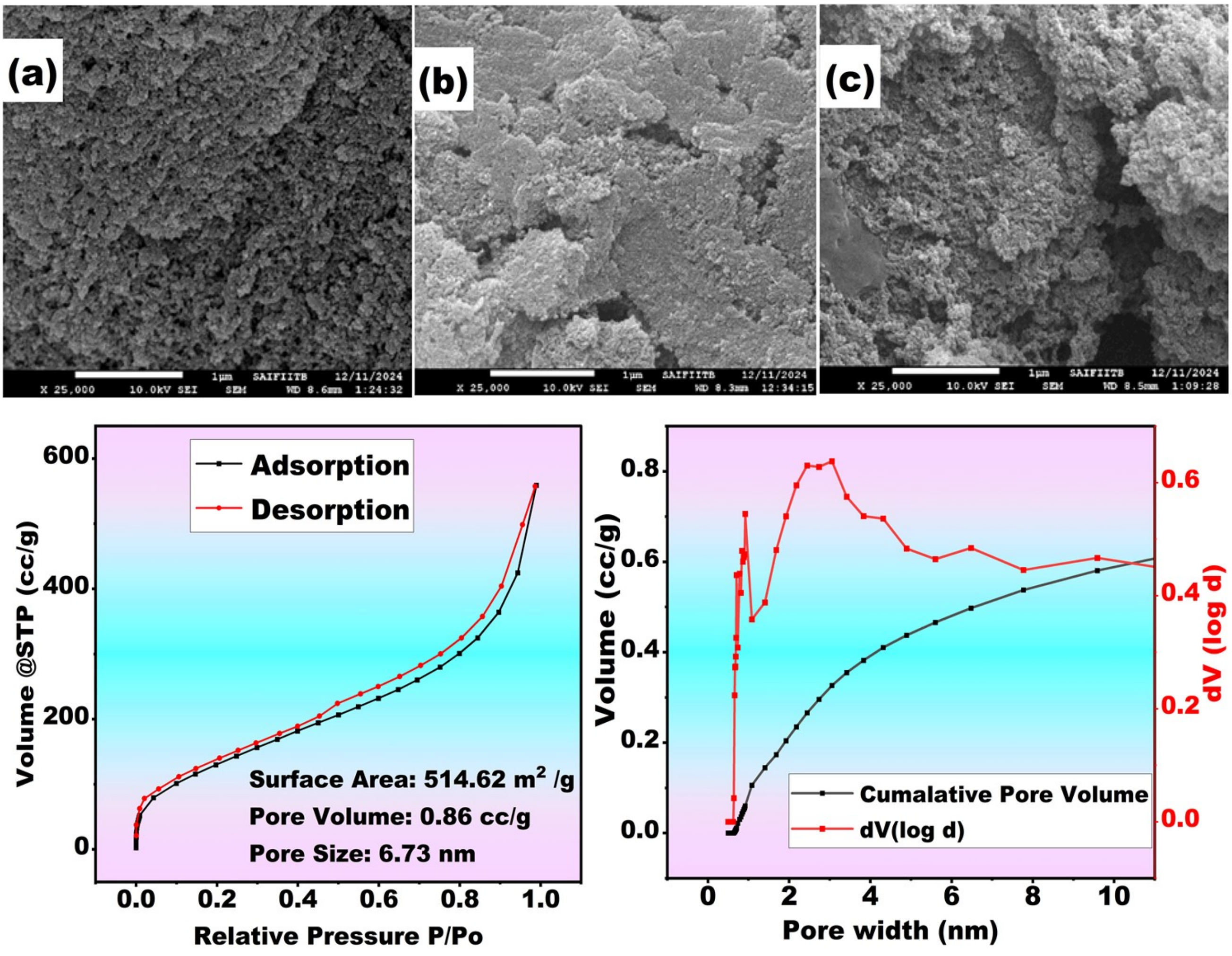


Figure S3: FEG-SEM image of (a) Fresh adsorbent, (b) PFCAs loaded adsorbent, and (c) regenerated adsorbent along with Nitrogen adsorption desorption plot (BET analysis)

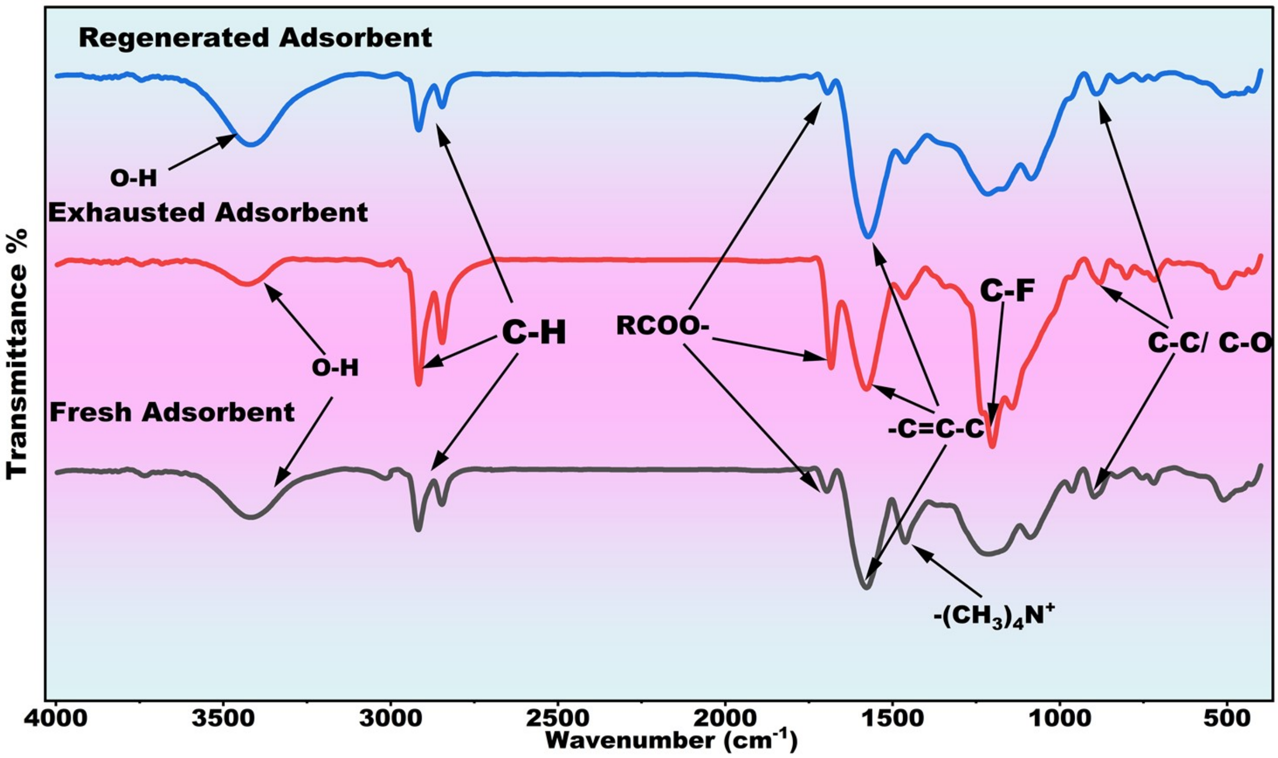
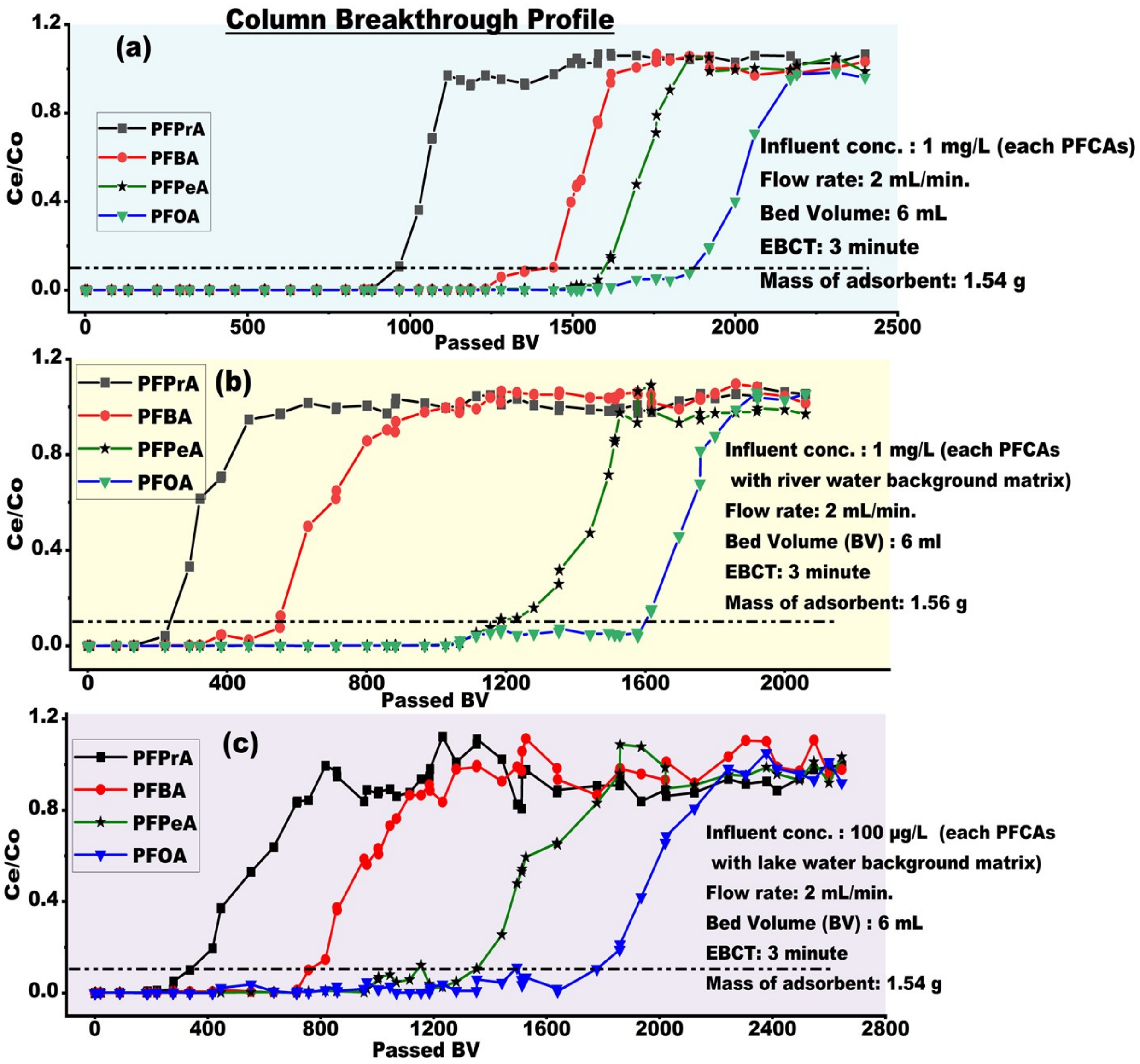


Figure S4: FTIR spectra of Fresh adsorbent, exhausted adsorbent, and regenerated adsorbent.



Column Breakthrough Profile

Influent conc. : 1 mg/L (each PFCAs)
Flow rate: 2 mL/min.
Bed Volume: 6 mL
EBCT: 3 minute
Mass of adsorbent: 1.54 g

Influent conc. : 1 mg/L (each PFCAs with river water background matrix)
Flow rate: 2 mL/min.
Bed Volume (BV) : 6 ml
EBCT: 3 minute
Mass of adsorbent: 1.56 g

Influent conc. : 100 µg/L (each PFCAs with lake water background matrix)
Flow rate: 2 mL/min.
Bed Volume (BV) : 6 mL
EBCT: 3 minute
Mass of adsorbent: 1.54 g

Fig. S5: Breakthrough profiles of individual PFCA adsorption with background of (a) DI water, (b) river water, and (c) lake water.

References:

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2. Inglezakis VJ, Poulopoulos SG. *Adsorption, Ion Exchange and Catalysis: Design of Operations and Environmental Applications*.; 2006. doi:10.1016/B978-0-444-52783-7.X5000-9

3. Ravikumar P, Aneesul Mehmood M, Somashekar RK. Water quality index to determine the surface water quality of Sankey tank and Mallathahalli lake, Bangalore urban district, Karnataka, India. *Appl Water Sci*. 2013;3(1). doi:10.1007/s13201-013-0077-2