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Sorption of perfluorinated compounds onto different types of sludge

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INTRODUCTION

Perfluorinated compounds (PFCs) consist by a hydrophobic perfluorinated carbon tail and a hydrophilic ionic headgroup. Because of their unique structure, PFCs have a wide variety of applications including active ingredient in fire fighting foams, impregnation for food packing and waterproof breathable fabrics (Scotchgard, Gore-Tex) and the producing of teflon.

Recently, the research interest for these compounds has been increased due to their recalcitrance, strong bioaccumulation and potential toxicity. While the occurrence of PFCs have been well documented in Sewage Treatment Plants (STPs) all over the world, however there is few data for their sorption potential to different types of sludge as well as for the mechanisms affecting this phenomenon. The aim of this work was to investigate the adsorption behavior of 5 PFCs (C8 to C11 carboxylic acids (PFCAs); and C8 sulfonic acids (PFASs)) in three types of sludge a) primary sludge, b) secondary sludge and c) anaerobic digested sludge. The solid-water distribution coefficient (K_d) values were determined for each PFC and different types of sludge in laboratory batch experiments. Furthermore, the influence of solution pH and ion strength on sorption were studied.

SAMPLING AND PREPARATION OF SLUDGE

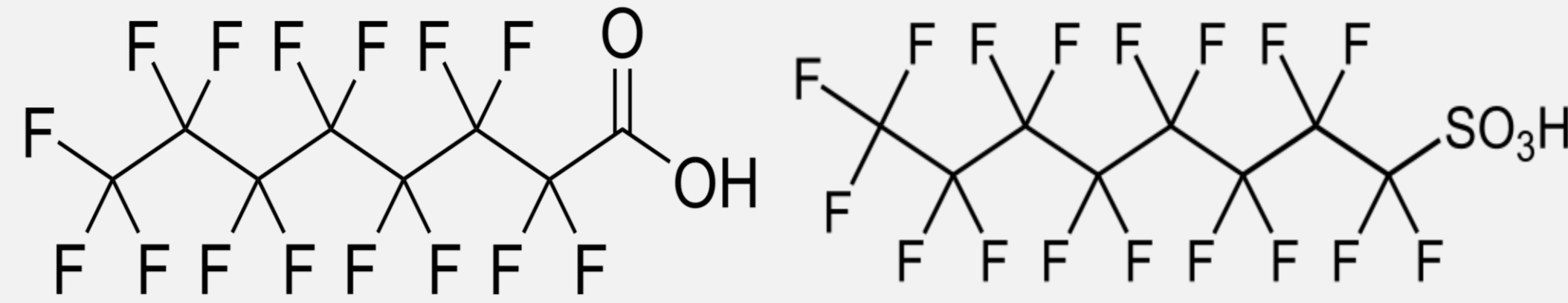
➤ Three type of sludge were collected from STP of Athens (Greece), which receives 750.000 m³ day⁻¹ wastewater and produces 120.000 Kg day⁻¹ dry solids. In this STP, activated sludge process operates at a HRT and SRT of 9 hours and 8 days, respectively; while sludge anaerobic digestion at a SRT of 20 days.

➤ All sludge samples were collected in high - density polyethylene bottles. Each type of sludge was washed three times using pure water and centrifuged. Remaining solids were frozen at -18 °C for at least 24 h. Freeze dry procedure was applied to preserve solids structure. Finally, solids were heated at 103 °C for minimum 3 h, in order to be sterilized and then stored at 4 °C.

➤ Characteristics of sludge used in these experiments are presented in Table 1.

Table 1. Sludge characteristics.

Parameters	Type of Sludge		
	Primary sludge	Secondary sludge	Digested sludge
Total Suspended Solids (g L ⁻¹)	7.0	6.0	24.9
Volatile Suspended Solids (g L ⁻¹)	6.0	5.2	18.3
pH	6.5	6.5	7.5
Conductivity (mS cm ⁻¹)	1.6	1.1	8.6
Loss On Ignition (%)	82.9	88.5	71.9
Oxidizable Organic Carbon (%)	46.8	36.0	34.5
Cl ⁻ (mg Kg ⁻¹)	108	79	108
Na ⁺ (mol L ⁻¹)	0.0003	0.0003	0.0003
Ca ²⁺ (mol L ⁻¹)	0.0004	0.0002	0.0015
Mg ²⁺ (mol L ⁻¹)	0.0001	0.0001	0.0003



EXPERIMENTAL SET UP

- Initially, the equilibrium time was investigated for each target compound using secondary sludge. Known amount of biomass (1 g L⁻¹) and target compounds (5 µg L⁻¹) were mixed in dark flasks to prevent possibly photodegradation. Samples were taken at predetermined time intervals (0, 4, 8, 12, 18, 24 h). Analysis was performed in the particulate phase and dissolved phase, to check sludge inactivation and find equilibrium time.
- Afterwards, sorption experiments were performed in triplicate using different types of sludge and different analytes' concentrations to calculate K_d values (Table 2).
- Finally, sorption experiments were performed with secondary sludge at different pH and concentrations of Na⁺ and Ca²⁺ (Table 2).
- Control experiments with no sludge were performed to exclude the role of other factors on PFCs removal (e.g. sorption on the flask). Blank samples were also analyzed to quantify background concentrations of each analyte.

Table 2. Description of sorption experiments (all experiments in triplicate).

Types	PFCs conc. (µg L ⁻¹)					pH	Na ⁺ / Ca ²⁺ (mM)
Primary sludge	0.2	0.4	0.8	1.5	3	5	
Secondary sludge	0.2	0.4	0.8	1.5	3	5	
				1.5			6, 7, 8
Digested sludge				1.5			1, 10, 100
	0.2	0.4	0.8	1.5	3	5	

ANALYTICAL METHOD

Table 3. Target compounds were used in this study.

PFCs	Systematic name	Emperic formula
PFOA	Perfluorooctanoic acid	C ₈ HF ₁₅ O ₂
PFNA	Perfluorononanoic acid	C ₉ HF ₁₇ O ₂
PFDA	Perfluorodecanoic acid	C ₁₀ HF ₁₉ O ₂
PFUdA	Perfluoroundecanoic acid	C ₁₁ HF ₂₁ O ₂
L-PFOS	Perfluorooctane sulfonate	C ₈ HF ₁₇ O ₃ S

Dissolved Phase	Particulate Phase
1. Solid Phase Extraction (Oasis HLB, 200 mg 6 cc)	1. Sonication (CH ₃ OH-CH ₃ COOH 1%)
2. Elution (4 mL MeOH)	2. Supernatant dilution to 50 mL H ₂ O
3. Evaporation to dryness	3. Solid Phase Extraction (Oasis HLB, 200 mg 6 cc)
	4. Analysis to LC-MS

Table 4. Instrumental parameters for the determination of PFCs.

LC - MS			
Agilent 1100 Series LC/MSD Trap			
Optimum Conditions			
Mobile Phase: (A) CH ₃ OH - (B) ammonium formate		Capillary Temperature: 350 °C,	
5 mM		Nebulizer gas: 30 psi,	
Column: X Terra MS, Waters, C18, (100x2.1 mm, 3.5 µm)		Dry gas: 8 L min ⁻¹	
Guard Column: Luna, Phenomenex, C18, (4x2.0 mm, 5 µm)		Flow rate: 0.1 mL min ⁻¹	
Gradient program:			
Time (min)	A (%)	Time (min)	A (%)
0	70	12	100
2	85	18	30

RESULTS AND DISCUSSION

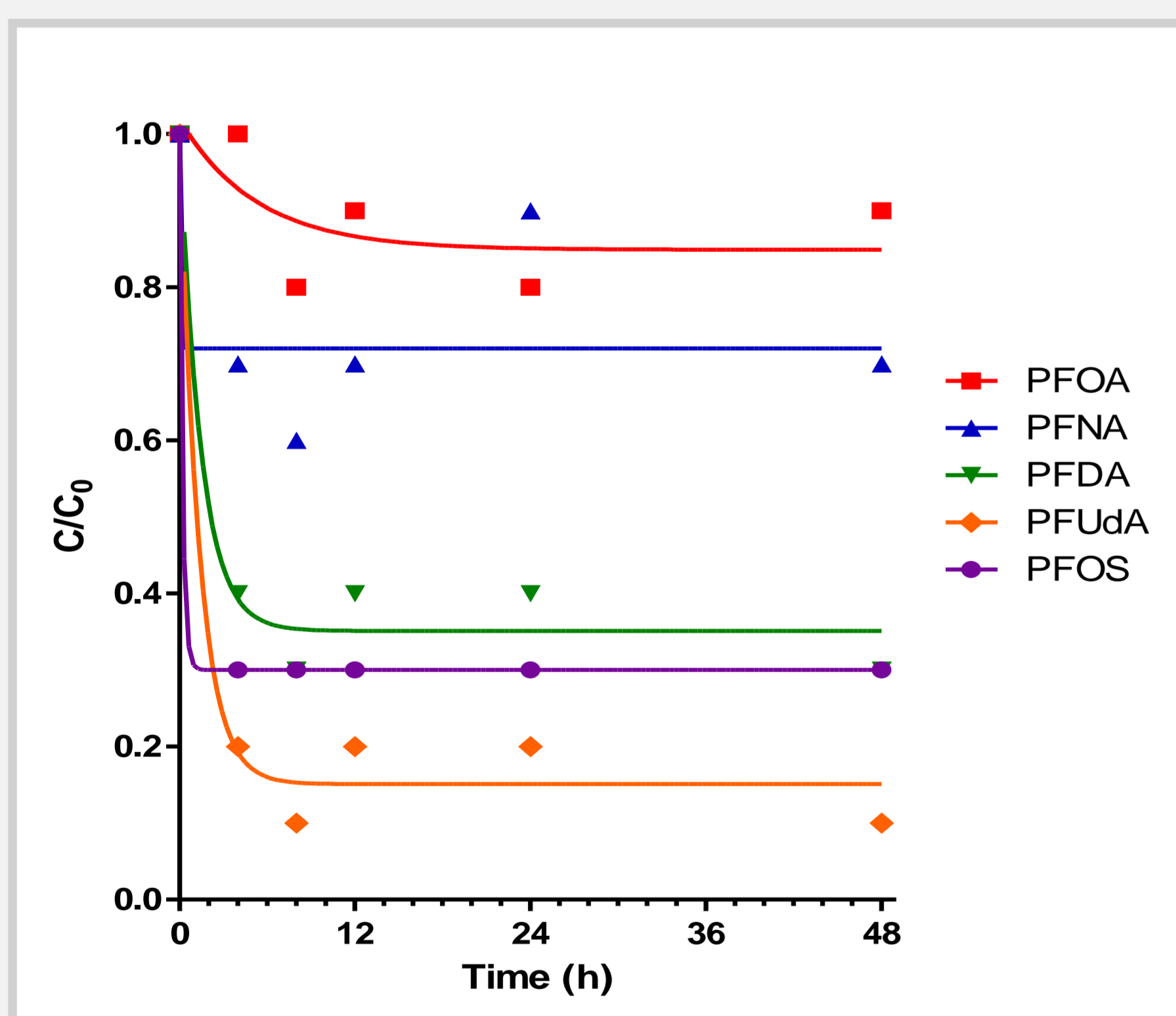


Figure 1. Equilibrium time of each target compound.

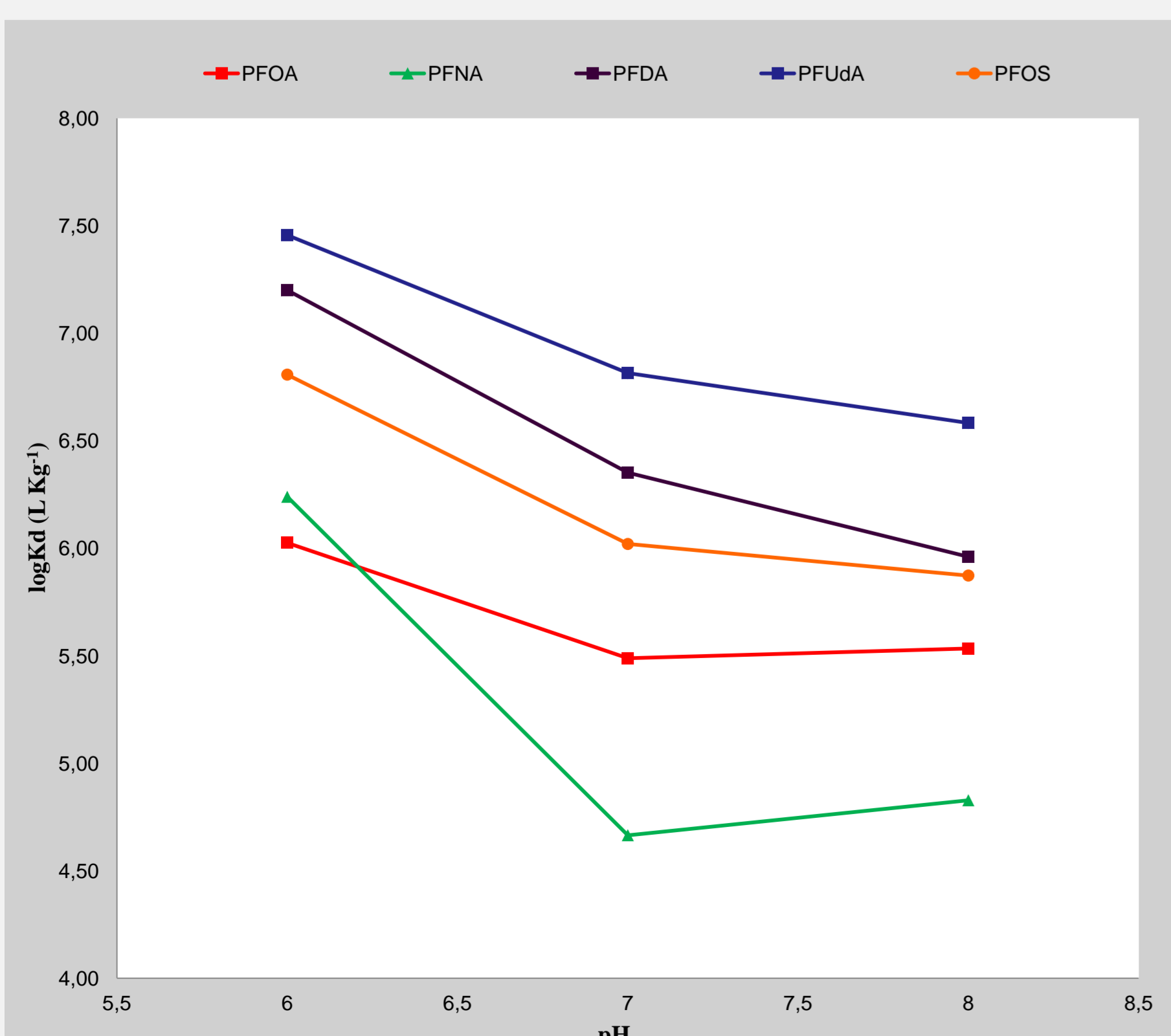


Figure 2. Effect of pH on the removal of PFCs.

- Sorption equilibrium was reached within 12 hours for all PFCs (Figure 1). The sum of masses on the dissolved and particulate phase was stable at all time intervals indicating no loss of compounds due to transformation and test vessel sorption (data not shown).
- Among different types of sludge, higher K_d values for all PFCs were determined for secondary sludge (Table 4). An increase of sorption was observed with increased CF-chain length for PFCAs (Table 4). Higher K_d -values were found for the sulfonate homologue, PFOS, comparing to the equivalent carboxylic acid (PFOA) (Table 4).
- The sorption of all PFCs increased with increase from pH 6.0 to 8.0 by 3- to 10-fold (Figure 2). The increase of Ca²⁺ concentration from 1 to 100 mM increased the sorption of PFCs (Figure 3) about 10-fold. No significant effect on sorption of PFC was observed for different Na⁺ concentrations (Figure 4).
- Measurements in control experiments (containing no sludge) shown no abiotic loss of the compounds (data no shown).

Table 4. K_d -values (L·Kg⁻¹) of PFCs for different types of sludge with 95%-confidence intervals.

PFCs	Primary sludge	Secondary sludge	Digested sludge
PFOA	281±27	444±226	183±87
PFNA	Not calculated	665±176	593±455
PFDA	4115±2717	5890±2686	4411±1408
PFUdA	16473±10503	24159±5606	14398±3563
L-PFOS	1876±531	3318±435	1947±435

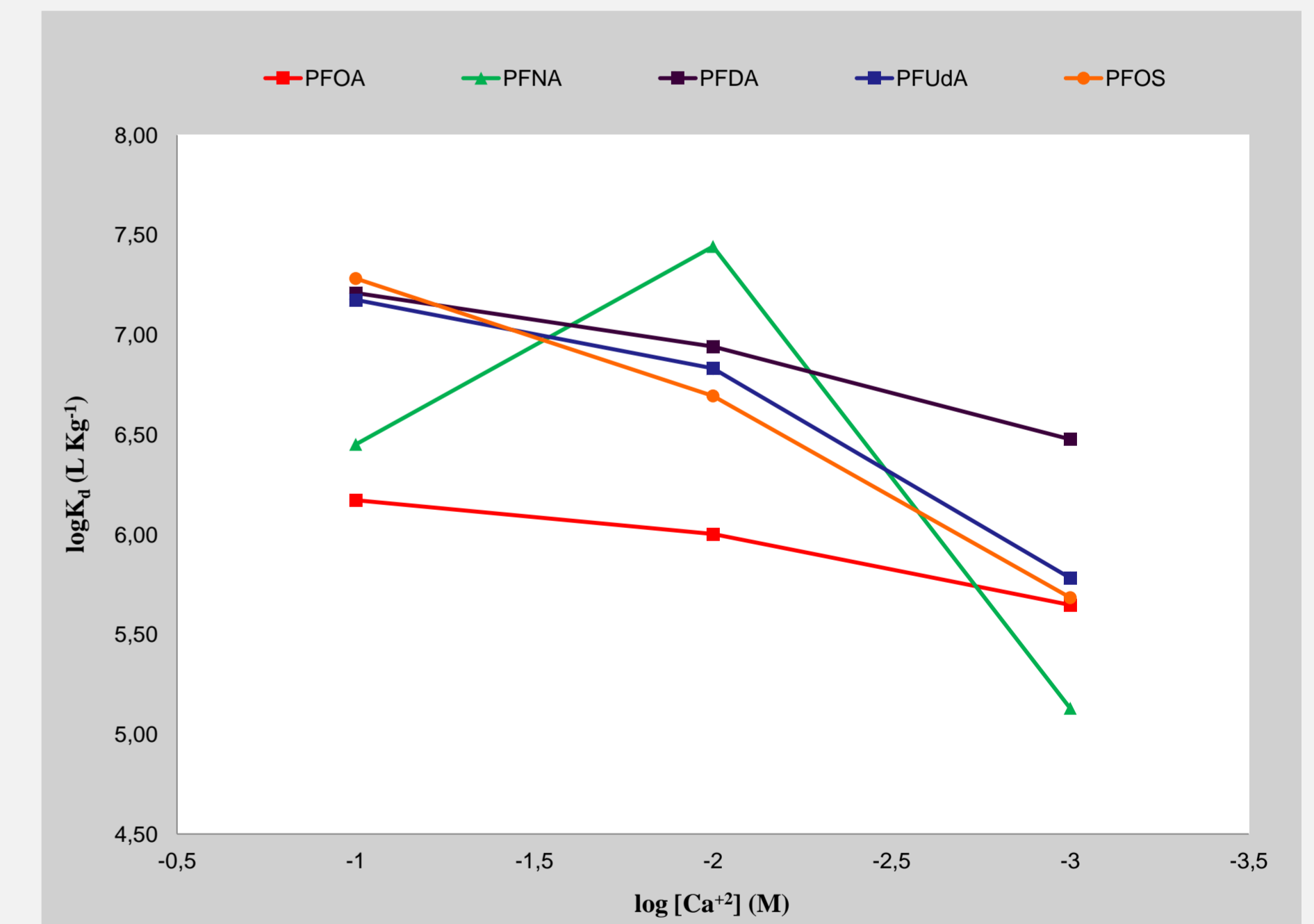


Figure 3. Effect of Ca²⁺ on the removal of PFCs.

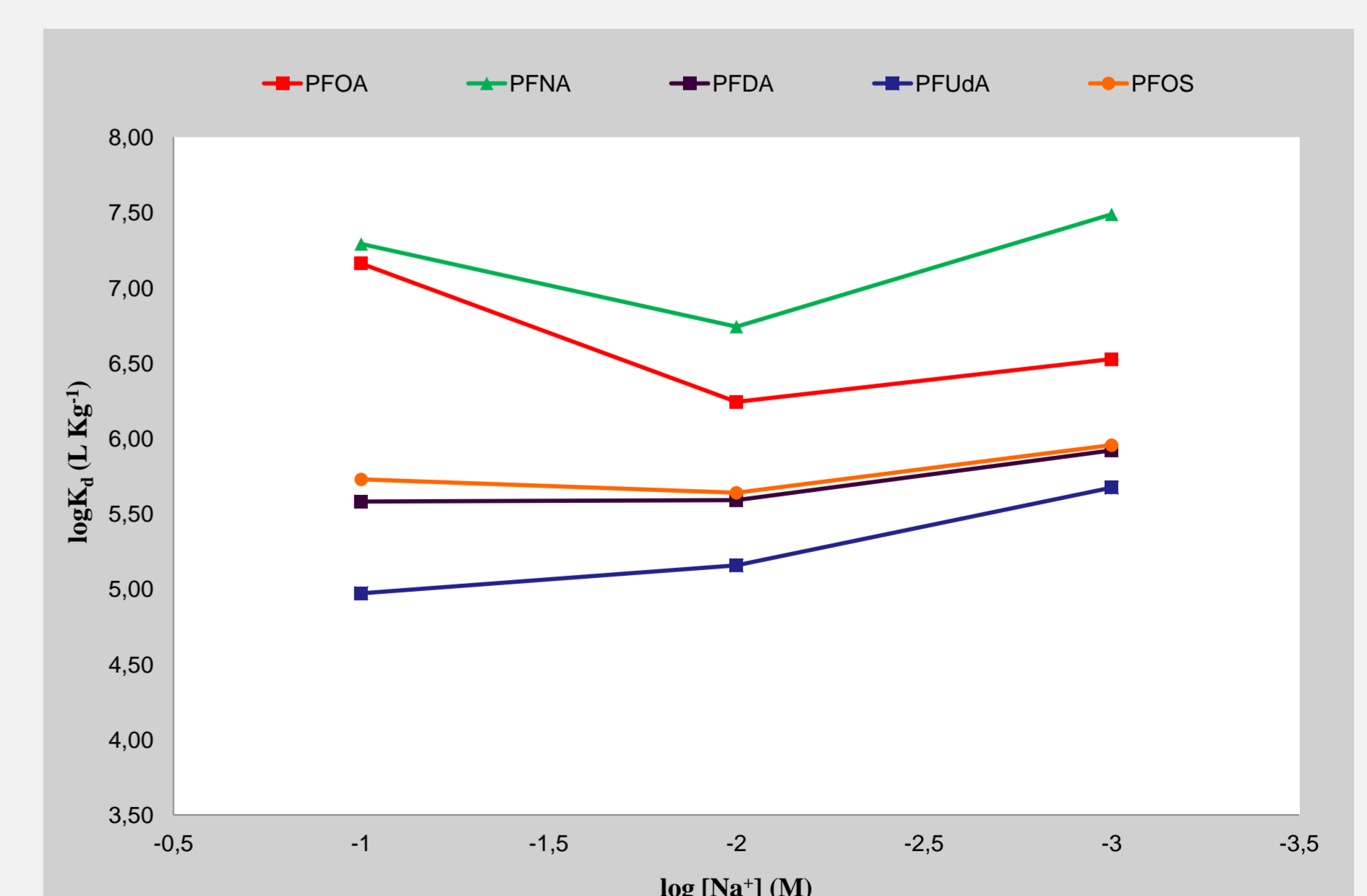


Figure 4. Effect of Na⁺ on the removal of PFCs.

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