


5-2020

Mesoporous Adsorbents for Perfluorinated Compounds

Bertha Lotsi
East Tennessee State University

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Mesoporous Adsorbents for Perfluorinated Compounds

A thesis

presented to

the faculty of the department of chemistry

East Tennessee State University

In partial fulfillment

of the requirements for the degree

Master of Science in Chemistry

by

Bertha Lotsi

May 2020

Dr. Aleksey N Vasiliev, Chair

Dr. Abbas Shilabin

Dr. Hua Mei

Keywords: Bridged silsesquioxanes; Sol-gel synthesis; Water treatment; Perfluorinated compounds

ABSTRACT

Mesoporous Adsorbents for Perfluorinated Compounds

by

Bertha Lotsi

Effective adsorbents for polyfluorinated compounds (PFCs) were successfully prepared. And they were tested in the adsorption of perfluorooctanoic and perfluorooctanesulfonic acids. Bridged silsesquioxanes containing secondary and tertiary amino groups were synthesized by sol-gel condensation of bis[3-(trimethoxysilyl)propyl]amine and bis[3-(methylamino)propyl]-trimethoxysilane in acidic media with surfactants. Obtained materials are mesoporous with high BET surface area. They combine high structural stability with a high concentration of surface amino groups serving as adsorption sites. Batch adsorption tests demonstrated their extremely high adsorption capacity on PFCs: in some experiments, it reached up to 88% of the adsorbent weight. Adsorption of PFCs changed the surfaces of the adsorbent nanoparticles from hydrophilic to hydrophobic thus providing their agglomeration and floatability. Column tests showed fast adsorption of PFCs even at high concentrations and high flow rates. Obtained results can be used in the development of an effective filtration device for clean-up of water contaminated by PFCs.

DEDICATION

I dedicate this thesis to the Almighty God for His protection on my life and to the Lotsi family.

ACKNOWLEDGEMENTS

I would like to thank Dr. Aleksey Vasiliev for giving me such an opportunity to be a part of his research group. Indeed, it has been an insightful journey which would be helpful in my future endeavors

I would like to thank Dr. Abbas Shilabin for being a part of my Advisory Committee, his advice, and help on organic chemistry.

I would like to thank Dr. Hua Mei for being a part of my Advisory Committee and all her help with my Thesis.

I would like to thank Dr. Reza Mohseni for all his help on the use of instrumentation from the beginning of my project to the end.

I would like to thank Anastasia Kuvayskaya and Esther Alorkpa for being such good research colleagues. The entire project could not have been successful without them.

The U.S. Environmental Protection Agency sponsored this project.

TABLE OF CONTENTS

ABSTRACT.....	2
DEDICATION.....	3
ACKNOWLEDGEMENTS.....	4
TABLE OF CONTENTS.....	7
LIST OF TABLES.....	8
LIST OF FIGURES.....	9
LIST OF ABBREVIATIONS.....	11
CHAPTER 1. INTRODUCTION.....	12
Perfluorinated compounds (PFCs).....	12
Adsorbents for PFCs Removal.....	15
Activated carbon.....	16
Resins.....	17
Mineral Materials.....	18
Biomaterials.....	19
Molecularly Imprinted Polymers.....	19
Adsorption Behavior of PFCs.....	20
Adsorption Kinetics.....	20
Adsorption Isotherm.....	21
Effect of solution chemistry.....	21
Effect of Adsorbent properties.....	22
Effect of PFCs properties.....	23
Mechanism of PFCs Adsorption.....	23
Electrostatic Interaction.....	23
Hydrophobic Interaction.....	24

Ligand and Ion exchange.....	25
Hydrogen Bond.....	25
Mesoporous Bridged Amino functionalized Polysilsesquioxane.....	26
Polysilsesquioxanes.....	26
Sol-gel chemistry.....	26
Bridged Polysilsesquioxanes.....	27
Objectives of the Project.....	28
CHAPTER 2. EXPERIMENTAL METHODS.....	29
Chemicals and Reagents.....	29
Synthesis of Materials.....	30
Adsorption Methodology.....	31
Batch test.....	31
Adsorption Isotherms.....	32
Column Tests.....	32
Regeneration.....	32
Instrumental Analysis and Characterization.....	32
Elemental Analysis.....	32
¹⁹ FNMR Spectra.....	33
FT-IR Spectra.....	33
Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).....	33
Particle Size.....	33
Brunnauer- Emmett- Teller (BET) Surface Area.....	33
TEM Imaging.....	34
CHAPTER 3. RESULTS.....	35
Synthesis of BSSOs.....	35

Adsorption of PFCs.....	35
Batch Test.....	35
Regeneration.....	38
Adsorption Isotherm.....	39
Column Tests.....	40
Flow Rate.....	40
FT-IR Spectra Analysis.....	41
Thermoanalysis.....	43
Dynamic Light Scattering.....	43
Porosimetry.....	45
TEM Imaging.....	45
CHAPTER 4. DISCUSSION.....	50
Conclusion.....	50
REFERENCES.....	56
VITA.....	57

LIST OF TABLES

Table 1. Physicochemical Properties of PFOA and PFOS	13
Table 2. PFCs Concentration Guidelines from US-EPA and Some States	15
Table 3. Properties of Chemicals and Reagents used.....	29
Table 4. Preparation of Samples 1-8 with Respective Precursors and Surfactants.....	31
Table 5. Results of Elemental Composition, Yield, the Content of Amino Groups and Loading of Amino Groups of Samples 1-8	36
Table 6. The Particle Size Distribution of Samples 1-8 Before and After Adsorption of PFOA/PFOS	44
Table 7. BET Surface Area of Samples 1-8 Before and After Adsorption of PFOA/PFOS.....	46

LIST OF FIGURES

Figure 1. Hydrologic unit codes used as a proxy for watersheds with detectable PFOA and PFOS in drinking water (2013-2015).....	14
Figure 2. Electrostatic attraction and repulsion of PFCs on various adsorbent site.....	24
Figure 3. Hydrophobic interactions of PFCs on various adsorbent site.....	25
Figure 4. A typical polycondensation of TEOS.....	27
Figure 5. A monomeric building block, bis[3-(trimethoxysilyl)-methyl] amine used as a precursor to bridged-polysilsesquioxanes.....	28
Figure 6. Structure of TMPA.....	29
Figure 7. Structure of MAPS.....	30
Figure 8. Structure of PLU.....	30
Figure 9. Adsorption of PFOA and PFOS by various adsorbents, Sample 1-8	37
Figure 10. The synthesized adsorbent in water before (a) and after (b) adsorption of PFOA.....	37
Figure 11. Regeneration of samples 1 and 5 containing adsorbed PFCs.....	38
Figure 12. Isotherms of adsorption of PFOA and PFOS on materials 1 and 5 and linear fitting plots of Freundlich isotherm models at different temperatures (°C): 2 (■), 30 (●), and 40(▲)	39
Figure 13. Column tests on samples 1 and 5	40
Figure 14. Effect of flow rate on the adsorption of PFOA and PFOS.....	41
Figure 15. FT-IR spectra of 1 and 5 before and after adsorption	42
Figure 16. FT-IR spectra for PFOA.....	42
Figure 17. DCS and TGA curves of 1 before and after adsorption of PFOA.....	44
Figure 18. Particle size distribution of 1 before and after adsorption.....	44
Figure 19. TEM Imaging for sample 1 and 5 in 0.5 μm and 10 nm	45

LIST OF ABBREVIATIONS

AC	Activated Carbon
AFFFs	Aqueous Film-Forming Foams
BET	Brunauer-Emmett-Teller Theory
BSSOs	Bridged Silsesquioxanes
CD	Cyclodextrin
DDA	Dodecyl Amine
DSC	Differential Scanning Calorimetry
¹⁹ F-NMR	Fluorine-19 Nuclear Magnetic Resonance
FT-IR	Fourier Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
HCl	Hydrochloric Acid
HDTMAB	Hexadecyltrimethyl Ammonium Bromide
MAPS	Bis[3-(methylamino) propyl]trimethoxysilane
MIPs	Molecularly Imprinted Polymers
NOMs	Natural Organic Matters
PAC	Powdered Activated Carbon
PFCs	Perfluorinated Compounds
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonate
PLU	Pluronic P123
SDBS	Sodium Dodecyl Benzenesulfonate
SDS	Sodium Dodecyl Sulfate
TEM	Transmission Electron Microscopy
TEOS	Tetraethoxysilane

TFMSA	Trifluoromethanesulfonic Acid
TGA	Thermogravimetric Analysis
TMPA	Bis[3-(trimethoxysilyl) propyl]amine
TMS	Trimethyl Stearyl Ammonium Chloride
US-EPA	United States Environmental Protection Agency

CHAPTER 1. INTRODUCTION

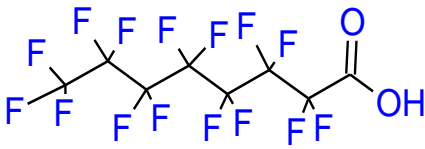
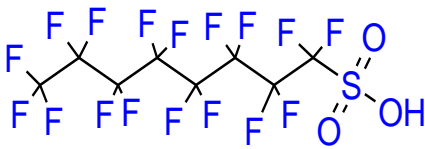
Perfluorinated Compounds (PFCs)

Perfluorinated compounds (PFCs), also known as the Perfluoroalkyl substances (PFASs)¹ are anthropogenic (generated from human activities) organo-fluorine compounds. The hydrogen atoms in the hydrocarbon backbone are replaced by fluorine atoms.² PFCs have the characteristics such as amphiphilic (the ability to possess both hydrophilic and hydrophobic properties), making them accessible in the applications of papermaking, firefighting foams,³ photolithography, and in the production of semiconductors. The carbon-fluorine (C-F) bond in fluorocarbons has sufficiently high energy (110 kcal/mol). It provides chemical stability of PFCs; hence they are persistent and widely spread in the aquatic environments.

PFCs come in many forms, but the two commonly known ones are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). In recent times, the manufacturing and use of PFCs are limited in the United States, Canada, and Europe.⁴ The bioaccumulative nature of PFCs makes it a requirement for researchers to find technologies for their removal from the environment, especially in water bodies.

Throughout decades PFCs are produced and disposed about in large amounts from manufacturing companies contaminating agricultural produce and mostly waterbodies. The most persistent of PFCs are PFOA and PFOS. Precisely, PFOS was used in the production of clothes, furniture, and carpet in the United States until the 2000s. And PFOA is still in use for the formation of stainless-steel cookware.⁵ One can get exposed to PFCs from food packagings such as pizza boxes and microwave popcorn bags. PFCs can also be present in products such as textiles.⁶ Table 1 shows the structures and some properties of PFOA/PFOS in literature.

Table 1. Physicochemical Properties of PFOA and PFOS ²

PFC	Structure	M.W. (g/mol)	pKa	Solubility in water (mg/L)	Molar volume (cm ³ /mol)
Perfluorooctanoic acid (PFOA) CF ₃ (CF ₂) ₆ COOH		414.17	2.5	3400	256
Perfluorooctane-sulfonic acid (PFOS) CF ₃ (CF ₂) ₇ SO ₃ H		500.13	-3.27	570	257

Humankind should be concerned with PFCs because researchers have found serious health implications associated with the exposure of PFCs, i.e., cancer.^{7,8} Research has shown that the current thyroid disease records in the USA come from the high PFOS/PFOA concentration.⁹ The PFCs also cause reproduction problems, kidney and liver damage in laboratory animals. The half-life of PFOA in humans is close to 3 years, while in the case of PFOS it is a little above 3 years.¹⁰ Exposure of PFOA/PFOS caused low birth weight in laboratory animals, likewise in humans. It is essential that to reduce PFCs in the environment, we stay away from or limit the use of products containing these compounds.

PFCs have high solubility in aqueous solutions, and this is a serious concern because of the exposure of consumers to contaminated drinking water. In the US, drinking and waste-water bodies close to industrial sites that manufacture and use PFCs have been reported to contain higher concentrations of PFCs. Also, during firefighting training, aqueous film-forming foams (AFFFs), which contains PFCs, are disposed-off into the surroundings; aircrafts hydraulic fuels also contain PFCs. Therefore, water bodies close to civilian airports, firefighting training

centers, and PFCs manufacturing sites possessed high concentrations of PFCs. The white areas in the maps, (Figure 1) represent regions where no data was available.

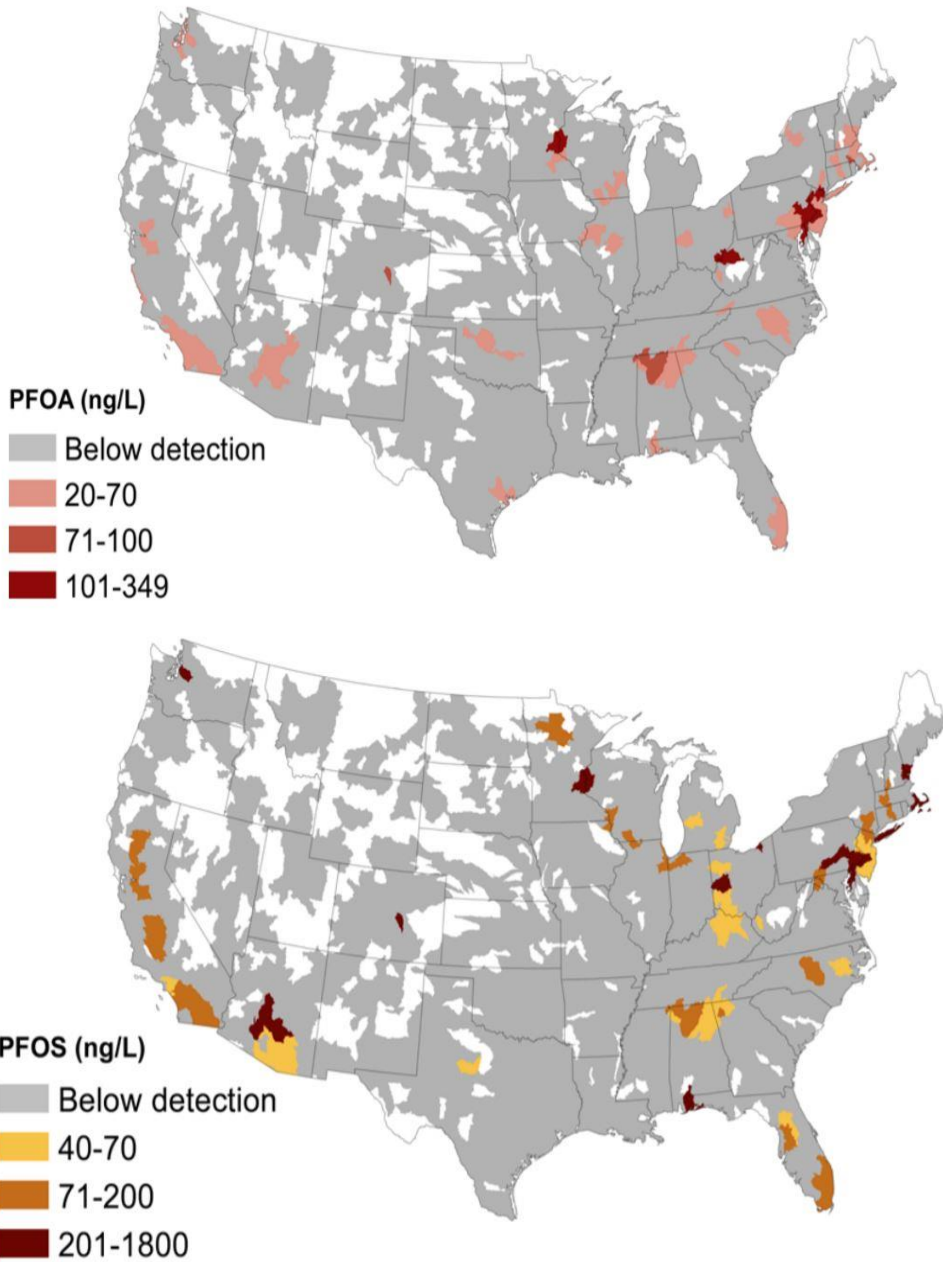


Figure 1. Hydrologic unit codes used as a proxy for watersheds with detectable PFOA and PFOS in drinking water (2013-2015) ¹

The US-EPA health advisory sector has a maximum concentration limit of PFOA/PFOS contaminants and is expected not to exceed 0.07 µg/L, especially in drinking water. Some water bodies close to sites where PFCs were used or manufactured contain up to ten folds of 0.07 µg/L. Table 2 shows some states in the US with guidelines on the concentration limits of PFOA/PFOS in their ground, surface, and drinking water.

Table 2. PFCs Concentration Guidelines from US-EPA and Some States ⁵

Agency or state	Matrix	Contaminant (µg/L)	
		PFOA	PFOS
US EPA	Drinking water	Lifetime health advisory: 0.070 (combined or individually)	
Illinois	Groundwater	0.400	0.200
Maine	Groundwater	0.060	0.100
Michigan	Surface water	0.420	0.012
Minnesota	Drinking water and fish consumption	0.610 (lake)	0.012 (lake)
		0.720 (river)	0.006 (river)
New Jersey	Drinking water	0.040	-
North Carolina	Groundwater	2	-
Vermont	Drinking water	0.020	-

Adsorbents for PFCs Removal

There have been many effective removal techniques for PFCs from water bodies, such as thermal degradation,¹¹ photolysis, reverse osmosis, ultraviolet irradiation,¹² advanced oxidation processes. Adsorption is both practical and economical, making it one of the most used methods for the removal of PFCs from water bodies.

Adsorption is the accumulation of atoms, ions, or molecules from a gas, liquid, or dissolved solids known to be the adsorbate (e.g., PFCs) on either the liquid or solid surface of an adsorbent. A suitable adsorbent should possess a quality such as an intrinsic surface that is highly adsorbing. Its pore sizes must be regular and easily tunable. Also, its volume must be large enough, meaning the pore sizes can be modified. The following are some adsorbents used for PFCs removal.

Activated Carbon

Activated carbon (AC) is one of the most assuring adsorbents for the removal of PFCs from wastewater and even drinking water bodies such as groundwater and reservoirs.¹³ AC has a nonpolar surface, therefore used for removing hydrophobic pollutants. AC is also known for the removal of taste, odor, natural organic, and synthetic organic chemical compounds from water bodies, especially drinking water. AC materials are highly porous, and this provides a much larger surface area for the PFOA/PFOS to be adsorbed. There are two types of activated carbon, the powdered activated carbon (PAC) and the granular activated carbon (GAC). PAC mostly comes from materials that contain high carbon content such as coal and wood. PAC particles have a diameter of 0.1 mm or less, and both the density and the diameter ranges are affected by the type of material used for their production. GAC has a slow adsorption rate, and in most cases, the operational time exceed the estimated time. Comparing the two types of activated carbon, PAC has a higher adsorption capacity than GAC. AC is less expensive as compared to other types of adsorbent, and it can effectively adsorb PFOS/PFOA.

AC falls short when it comes to the regeneration of the adsorbent for reuse, and even the regeneration of GAC requires thermal methods. It is usually hard to use pure organic solvents (methanol or ethanol) to regenerate the adsorbent, and this makes it problematic for safe

disposal. The best way for the regeneration of this adsorbent is to wait for the PFCs to decompose, but PFCs do not decompose quickly due to their high stability, hence the need to use catalytic degradation to enhance their decomposition exists. When using AC as adsorbent, pH, contact time, and temperature comes into consideration for effective adsorption. One disadvantage with AC is that during the adsorption of PFCs, especially in groundwater, they end up adsorbing some natural organic compounds as well. Those natural organic compounds usually will compete for adsorption sites with the PFCs.

Resins

Resins have favorable physicochemical stability, larger adsorption capacity, good selectivity, structural diversity, and benefit of generation.¹⁴ The anion exchange resins have records showing highest adsorption capacity among the nonionic exchange resins. Research shows that PFCs are mostly present as anions in aqueous solution; this makes anionic exchange resin a useful material for PFCs removal.¹⁵ Even though anionic exchange resins are capable of adsorbing PFCs, the rate of their adsorption mostly depends on material porosity and the matrix of the polymer.

However, there is anionic competition, that is, if the contaminated water contains any other anions aside PFCs. Also, the short-chain PFCs are less effective with resins.¹⁶ Resins are highly expensive, hence the need to regenerate for reuse in PFCs removal. Resin can be regenerated onsite and this gives it a more economic advantage than an adsorbent such as GAC. Pure methanol can be used to regenerate already used nonionic resins. A mixture of methanol and salt solution is used for the regeneration of anionic exchange resin. Solvent elution is one method used for regeneration of the resins. Also, solvent washing is another simple technique that is used to regenerate resins, this potentially recovers the solute. The volatility and toxicity of

organic adsorbents make them dangerous to regenerate in situ. Acid deposition and salting-out are the examples of some conventional methods used in the removal of concentrated acidic PFCs for proper disposal.

Mineral Materials

Since minerals are essential components of the soil and water system, they must be well investigated as adsorbents. Some common mineral materials used as the adsorbents for the removal of PFCs are zeolites, goethite, kaolinite, and Ottawa sand. Research on such adsorbents has shown good adsorption with a high pH of the solution. The non-electrostatic interactions are the predominant type of interaction in PFCs adsorption onto silica. The silicate surfaces are hydrophilic and can be modified with cationic component for adsorption to occur. The structural properties of different mineral materials can determine their adsorption mechanism. Alumina is one of the mineral adsorbents and is highly efficient due to acid-base nature towards charged components in water.

Boehmite is an aluminum oxide hydroxide. Its surface abundant with hydroxyl groups that cause it to have 2-3 times higher adsorption rate than γ -alumina material.¹⁷ To understand and generate a good result for most mineral materials, especially for goethite, alumina, silica adsorbents, pH change, ionic strength, and Ca^{2+} concentration of solution must be considered.¹⁸ The effectiveness of these mineral materials is lower as compared to that of ACs and resins. One advantage of mineral material is their ability to tune their mesopores. Their structures are changeable, making them suitable for better adsorption. Modifiers, such as hexadecyltrimethylammonium bromide (HDTMAB), (3-aminopropyl)-triethoxysilane, 1,8-bis(dimethylamino)naphthalene, and 1H,1H,7H-dodecafluoroheptyl methacrylate are loaded on these mineral materials to enhance their PFCs adsorption. They function by entering the inner

layers of these materials and thus increasing the intralayer spaces to affect PFCs adsorption. For mineral materials, the PFCs can be desorbed by the organic solvent washing method.

Biomaterials

Biomaterials are synthetic adsorbents formulated by researchers by mimicking natural types of adsorbents such as the AC. The idea was to decrease the adsorbent cost and to increase the adsorption capacity at PFCs removal. The biomaterial such as the crosslinked chitosan beads is less expensive but has high adsorption capacity for PFOS at low pH.¹⁹ The crosslinked chitosan is cheaper than resin and performs better in adsorption of PFCs than anion exchange resin. Biomaterials such as quaternized cotton and aminated rice husk originate from atom transfer radical polymerization.²⁰ They have amine groups on their surfaces and since these groups exhibit electrostatic attractive forces with anionic PFCs, this gives them high adsorption capacity. They also have unique abilities to adsorb PFCs at pH ranges of 5-9. It is hard to remove PFCs from aminated adsorbent with pure organic solvents, due to their strong adsorption affinity.

Molecularly Imprinted Polymers (MIPs)

PFCs removal from wastewater and water bodies requires materials with high selectivity. Due to many compounds competing with PFCs for adsorption sites, especially in wastewaters, adsorbents that are highly selective on PFCs are preferable.^{21,22} Due to this, some researchers have devised a technique called the molecular imprinting to manufacture molecularly imprinted polymers (MIPs). This method has high selectivity towards PFCs adsorption.²³

Some of the new MIPs prepared by researchers are chitosan crosslinked the epichlorohydrin and 4-vinyl pyridine with ethylene glycol dimethacrylate. For the imprinting effect of MIPs to be highly selective in the adsorption of PFCs, pH of the solution, the type of

template, the reaction time, and the quantity of crosslinking agents are surely come into consideration.²³ Some advantages of MIPs are the selectivity with PFCs, the ability to chemically tune them, mechanical strength and their high stability. Another type of MIPs is the cyclodextrin (CD) based polymer.²⁴ This type of MIPs has proven to be highly advantageous than the others, and it has multiple binding sites with exceptional physicochemical properties in varying shapes and forms.

Adsorption Behavior of PFCs

Every adsorbent has its peculiar and unique way of adsorbing the PFCs onto its surface. Adsorption behavior can be affected by solution chemistry (solution pH, inorganic ions, organic compounds), adsorption kinetics, adsorption isotherms, PFCs, and adsorbent properties.

Adsorption Kinetics

Adsorption kinetic is the measure of the amount of material adsorbed by an adsorbent concerning the time when pressure or concentration is constant. The three most common kinetics used to attribute to PFCs adsorption are, pseudo first order kinetic model, pseudo second order kinetic model and the intra-particle diffusion model. In order to calculate the diffusion of adsorbate (PFCs) in the pores of the adsorbent, the adsorption of the particle diameter and the pore size of the adsorbent must be considered since this determines the adsorption kinetics. Researchers have reported that PAC adsorbent exhibits faster adsorption rates of about 1-5 hours with adsorption capacity at equilibrium concentration of 100 mg/L.²⁵ For GAC adsorbent, it takes as long as about 168 hours for adsorption to complete.²⁶ For PFCs such as PFOA/PFOS, a mesoporous adsorbent shows higher adsorption rates than the others adsorbents. This is because a mesoporous adsorbent has better intraparticle diffusion rate.

Adsorption Isotherms

It is the graphical representation of the amount of an adsorbate adsorbed on an adsorbent at constant temperature and pressure. Researchers have admitted that, indeed, the Langmuir model properly explains the adsorption isotherm for PFCs. The most studied adsorption isotherms among PFCs are for PFOA and PFOS. The amine group-containing adsorbent, such as crosslinked chitosan, was purposely prepared, and the adsorption capacity for PFOA recorded to be the highest (2,745 mg/g). The anion exchange resin exhibited higher adsorption as well (2,575 mg/g for PFOS and 1,206 mg/g for PFOA), proving their excellent adsorption capacity. The nonionic resins showed low adsorption capacity, and their results were even lower than some AC. PAC had an adsorption capacity of 374-500 mg/g for PFOS and 175-524 mg/L for PFOA. The GAC had much lower adsorption capacity than the PAC, giving 160-229 mg/g for PFOS and 121-161 mg/g for PFOA.²⁵ The mineral materials showed inferior adsorption capacity, and these are silica, alumina, zeolites, and montmorillonite. For example, the inorganic alumina exhibited an adsorption capacity of 22.3 $\mu\text{g/g}$ for PFOS and 13.9 $\mu\text{g/g}$ for PFOA.

Effect of Solution Chemistry

In most cases, at high pH, PFCs adsorption is lower. But this case is not always valid, especially when certain divalent cations are present in the solution. Researchers explained that the increase PFCs adsorption capacity at high pH when cations such as Mg^{2+} and Ca^{2+} are present.^{27,28,29}

Inorganic cations or anions can affect PFCs adsorption either negatively or positively, causing surface charge neutralization, competitive adsorption, and divalent cation bridging effects. Divalent cations (Mg^{2+} and Ca^{2+}) can neutralize the negative surface of the adsorbent with an increase in zeta potential. They can form a bridge with phenolic, carboxyl, and hydroxyl

adsorbent groups, thus providing better adsorption.³⁰ Recorded, Mg^{2+} mostly forms a bridge with adsorbent of carboxyl groups while Ca^{2+} does with both the carboxyl and sulfonate groups.

Inorganic anions in solutions make the opposite effect. Instead they compete with the PFCs for adsorption sites. Examples of anions that inhibit adsorption of PFC are Cl^- , SO_4^{2-} , and $Cr_2O_7^{2-}$.

Organic compounds or Natural Organic Matter (NOMs) and organic pollutants compete for adsorption sites with PFCs, hence the primary cause for a competitive source for PFC adsorption. NOMs with the same molecular size as that of PFCs compete to occupy adsorption site and this decreases the adsorption capacity of PFC. Some surfactants, such as hexadecyltrimethylammonium bromide (HDTMAB) and sodium dodecyl benzenesulfonate (SDBS), at higher concentrations, inhibit the adsorption of PFCs. At high concentrations, these surfactants produce micelles which makes PFCs soluble hence decreasing the adsorption effect.³¹

Effect of Adsorbent Properties

There are different kinds of adsorbents with unique adsorption capacities and rates for PFCs removal. The properties of these adsorbents such as, particle size, pore size, and surface chemistry determine their way of adsorption.

Adsorbents of PFCs with different particle sizes result in various adsorption capacities. PAC with the particle size of less than 0.1 mm will tend to adsorb more PFCs on its surface than GAC with particle sizes between 0.9-1 mm. Adsorbents with bigger particle sizes usually reduce pore accessibility and the steric hindrances blocking PFCs adsorption.

As the scientist indicated, the macroporous anion-exchange resins have higher adsorption capacity for PFCs than the mesoporous resins. Due to the pore blockage effect, microporous zeolites have lower adsorption capacity for PFCs than mesoporous hexagonal silica.

The reason is that the mesoporous materials have more space to accept large PFCs molecules. Hence the pore size and surface area play essential roles in the selection of an adsorbent for PFCs removal.

Surface chemistry determines the effect of the adsorbent functional groups concerning PFCs. Research has shown that, for example, silica with different functional groups on its surfaces has different adsorption capacities. The more basic the functional group, such as a positively charged surface, the better it adsorbs anionic PFCs on its surface. Adsorbents with the multiple functional groups exhibit low adsorption capacity.

Effect of PFCs Properties

Reports show that PFCs have relatively low pKa values and exist as anions in waterbodies.³² Pearson's hard and soft bases explain that the sulfonate group is a hard base, while the carboxylate group is the soft base. Hence hard bases readily adsorb on the surfaces of hard acids (oxide surfaces), hence the reason for PFOS adsorption at higher capacities by silicas, ACs, and sediments than PFOA. Also, various adsorbents tend to adsorb higher amounts of PFCs with the increase in the number of C-F bonds with the same acidic group. With the longer C-F chain, PFCs have the lower water solubility. Hence the PFCs are more hydrophobic, and their capacity to be adsorbed is optimum when hydrophobic interaction is involved in the adsorption.

Mechanisms of PFCs Adsorption

Electrostatic Interaction

Most adsorption processes of adsorbents PAC and commercial thin- film composite polyamide membrane can occur through electrostatic interactions.^{33,34} Electrostatic attractions occur between the positively charged adsorbent surface and anions of PFCs. Metal cations (e.g.,

Mg²⁺) can catalyze anion adsorption, increasing electrostatic attraction between PFCs and the adsorbent. Anionic adsorbents mostly repel PFCs anions. NOMs are also anionic and are likely to resist most PFCs unless they are bridged or activated by other compounds. Figure 2 shows the different possibilities of electrostatic attraction and repulsion that can occur between adsorbents and PFCs.

(a) Electrostatic attraction



(b) Electrostatic repulsion

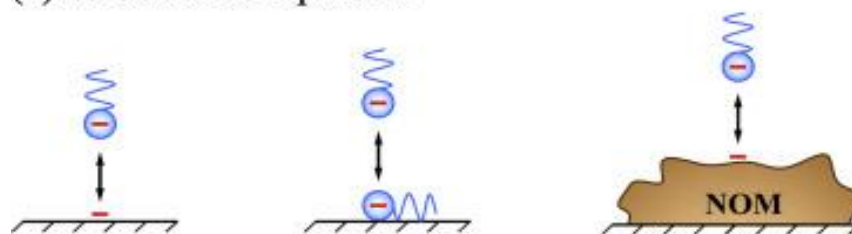


Figure 2. Electrostatic attraction and repulsion of PFCs on various adsorbent sites ²

Hydrophobic Interactions

PFCs can still be adsorbed on the negatively charged surface of the adsorbent by hydrophobic interactions. NOMs mostly found in aquatic environments act as hydrophobic parts for PFCs adsorption. Typically, PFOS and PFOA with a long perfluoroalkyl chains can form hemimicelles or micelles in water. When these hemimicelles and micelles collide, their tails can

amass together, and this brings high adsorption capacity.³⁵ Figure 3 explains some adsorbent surfaces and how hydrophobic interactions of PFCs occur on these surfaces.

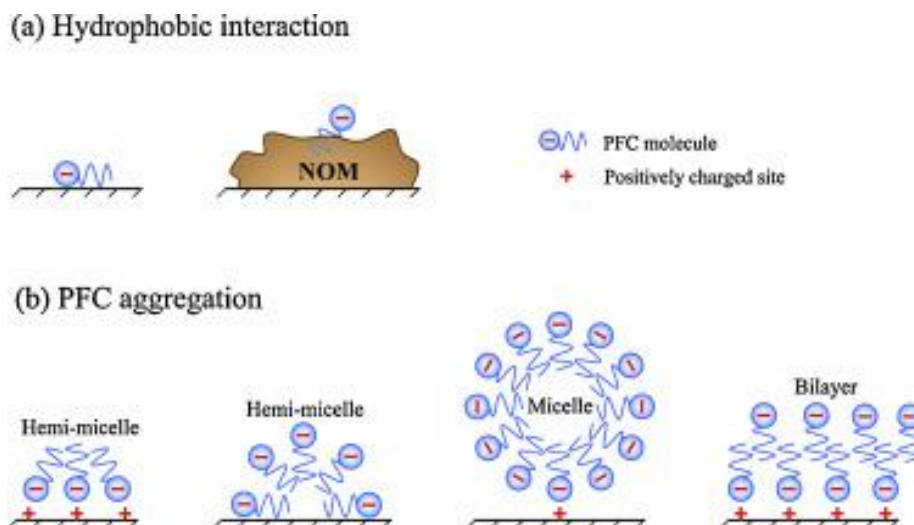


Figure 3. Hydrophobic interactions of PFCs on various adsorbent sites²

Ligand and Ion Exchange

Some adsorbents prefer to adsorb by interacting with the functional group heads of PFCs. The ion exchange resin, for example, using exchange interaction, release hydroxyl groups for PFCs. Research shows that anion exchange resin with Chloride on its surface can exchange the chloride with PFOS. Hence the ratio of PFOS adsorbed to Cl^- released ranging between 1-1.28, indicating that anion exchange reaction subjugated the adsorption of PFOS on resins.

Hydrogen Bonds

Due to the hydrophobic nature of the C-F bond, it is hard for PFCs to form hydrogen bonds with water molecules or other hydrogen-containing polar molecules.³⁶ Adsorbents with OH, COOH, and NH_2 groups do not form hydrogen bonds with PFCs. However, functional

group heads of PFCs contain oxygen atoms, which may form hydrogen bonds with OH, COOH, and NH₂ groups.

Mesoporous Bridged Amino-Functionalized Polysilsesquioxanes

The interest of this research is to use silsesquioxanes, a type of mineral material adsorbent, modify its surfaces with amine groups to purposely serve as the adsorption site for the removal of Perfluorinated compounds.

Polysilsesquioxanes

Polysilsesquioxanes are organosilicon compounds that comprise of silicon atoms bonded by oxygen molecules and R (where R could be H, alkyl, acyl, or alkoxy group). Their polymeric structures are mostly cage-like with Si-O-Si linkages. The silicon has tetrahedral vertices (3 oxygen molecules which also bonds with other silicon in the organic structure). This kind of material is quite uncommon because they have an inorganic silicate as its core and an external organic moiety.³⁷ The silica core of this compound confers rigidity and thermal stability. The material is suitable for precursors in nanocomposites.

Sol-Gel Chemistry

A common way to synthesize polysilsesquioxanes is the sol-gel method. An example is polymerization of tetraethoxysilane Si(OEt)₄ (TEOS), and the chemical steps involved are hydrolysis and condensation. These steps ensure the formation of Si-O-Si chemical linkages. In a typical sol-gel reaction, the acid or base acts as a catalyst. The silica polymers can grow until a gel transition ultimate, which can transform into a solid-like gel (Figure 4). The introduction of an organic group into this inorganic polymer can change its physical properties.³⁸

Bridged Polysilsesquioxanes

The bridged polysilsesquioxanes are highly cross-linked hybrid organic-inorganic materials. They contain variable organic fragments attached to the trialkoxysilyl groups. This kind of sol-gel polymerization leads to a network formation called bridged polysilsesquioxanes (Figure 5).³⁹ The importance of bridging is to develop the full potential of both the organic and inorganic group or moieties. The condensation polymers are covalently attached to the inorganic phase. An alkyltrimethoxysilane is bridged with an amino-functionalized group form a stable silsesquioxane with high porous surface.^{40,41}

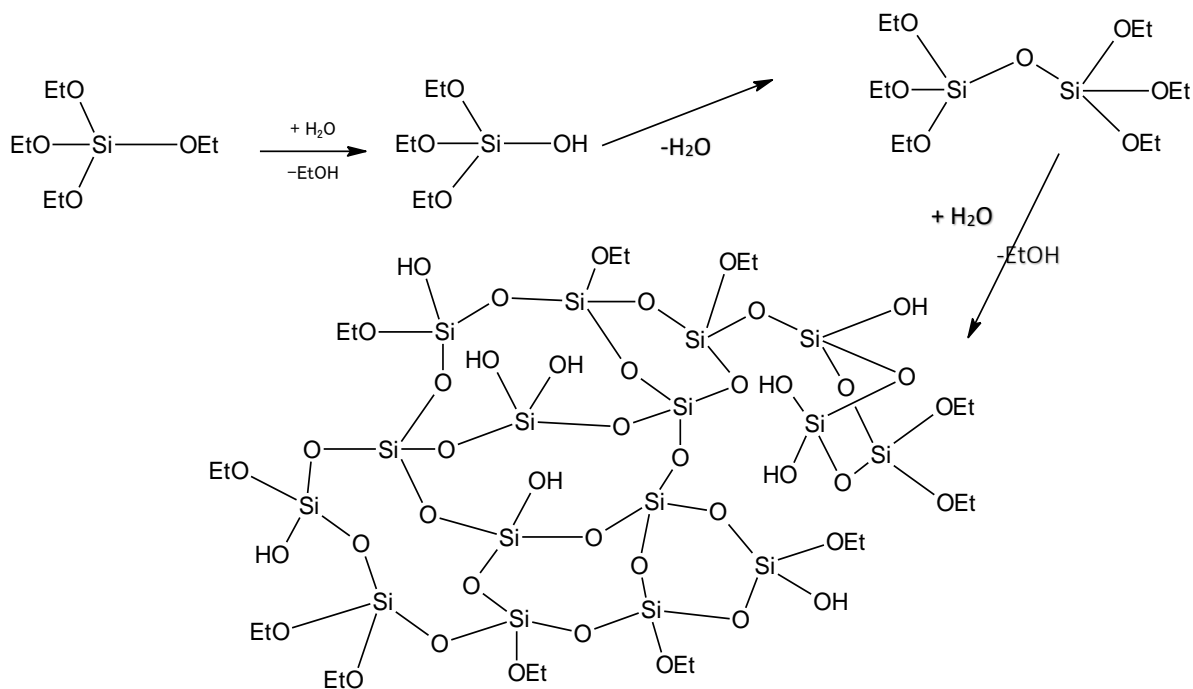


Figure 4. A typical polycondensation of TEOS

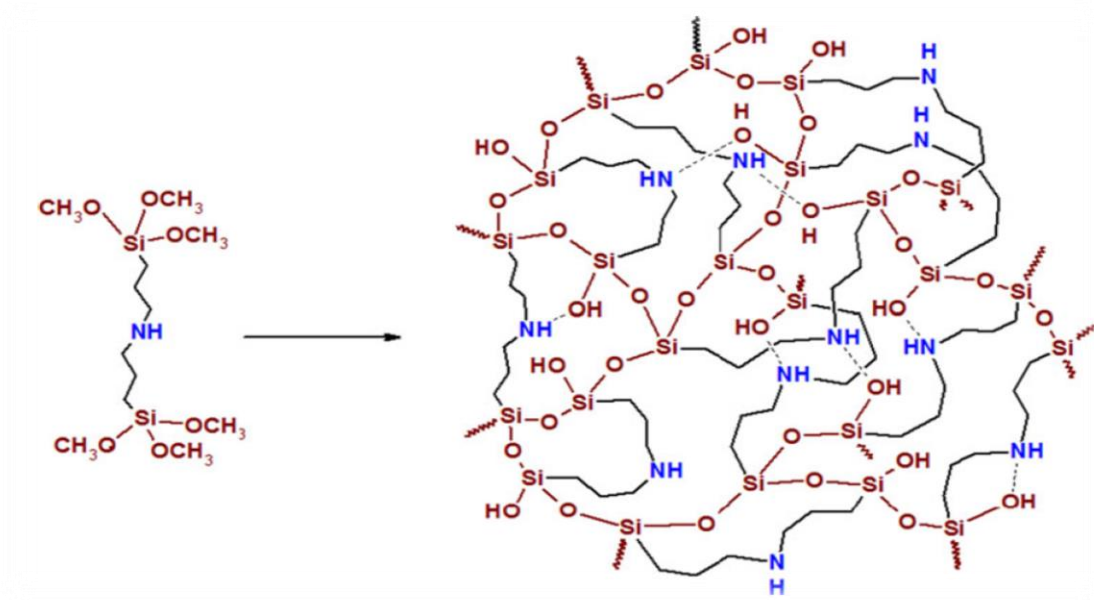


Figure 5. Synthesis of bridged polysilsesquioxanes from a precursor

Objective of the Project

The main objectives of this project are to synthesize effective adsorbents for PFCs removal from contaminated water. The synthesized environmentally friendly materials must be recyclable with high adsorption capacity on PFCs. Mesoporous bridged amino-functionalized silsesquioxanes were chosen as prospective materials due to their high surface area and contents of basic adsorption sites.

CHAPTER 2. EXPERIMENTAL METHODS

Chemicals and Reagents

Table 3 lists various chemicals and reagents used and their roles in the syntheses.

Table 3. Properties of Chemicals and Reagents Used

Name	Chemical formula	Manufacturer	Role
Bis[3-(trimethoxysilyl)-propyl]amine (TMPA)	See Figure 6	Sigma-Aldrich (St. Louis, MO)	Precursor
Bis[3-(methylamino)-propyl]trimethoxysilane (MAPS)	See Figure 7	Sigma-Aldrich	Precursor
Trimethylstearylammonium chloride (TMS)	$C_{18}H_{37}(CH_3)_3NCl$	TCI (Tokyo, Japan)	Surfactant
Dodecylamine (DDA)	$C_{12}H_{25}NH_2$	Acros Organics (Morris Plains, NJ)	Surfactant
Sodium dodecyl sulfate (SDS)	$C_{12}H_{25}SO_4Na$	Acros Organics	Surfactant
Pluronic P123 M.W. = 5800 (PLU)	See Figure 8	Sigma-Aldrich	Surfactant
Perfluorooctanoic acid (PFOA)	$C_7F_{15}COOH$	Sigma-Aldrich	PFC
Perfluorooctane sulfonate (PFOS) (40% in H_2O)	$C_8F_{17}SO_3H$	Sigma-Aldrich	PFC
Trifluoromethanesulfonic acid (TFMSA)	CF_3SO_3H	Acros Organics	Reference for NMR

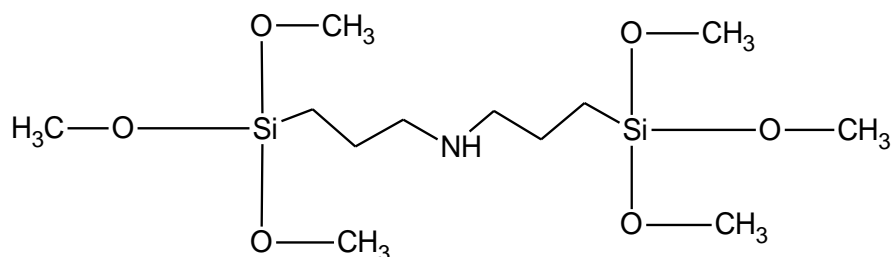


Figure 6. Structure of TMPA

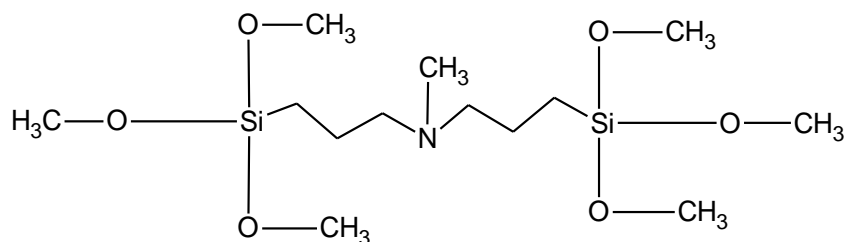


Figure 7. Structure of MAPS

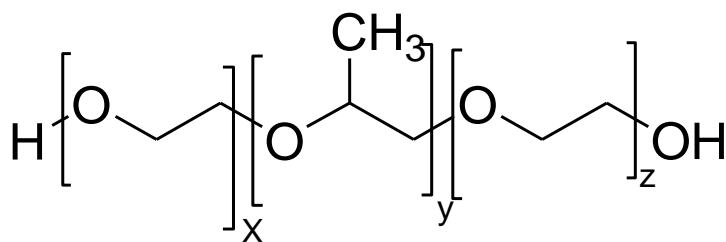


Figure 8. Structure of PLU

Synthesis of Materials

The sol-gel method was used for the synthesis of the adsorbents TMPA and MAPS by polycondensation. 2 g of a surfactant dissolved in 6 mL of ethanol. 3.2 g of a precursor dissolved in 2 mL of ethanol. As shown in Table 4, TMPA was used to prepare samples **1-4**, samples **5-8** were prepared using MAPS. Solutions of TMPA (MAPS) and 20% HCl were simultaneously added to the solution of surfactants dropwise under constant stirring. Shown in Table 4 are surfactants used for the preparation of these samples. The adsorbents were obtained by refluxing the reaction mixture for 24 h at 80°C. The gels were filtered, washed with deionized water and hot ethanol, rinsed with acetone and air-dried.

Table 4. Preparation of Samples **1-8** with Respective Precursors and Surfactants

Sample	Precursor	Surfactant
1	TMPA	TMS
2	TMPA	DDA
3	TMPA	SDS
4	TMPA	PLU
5	MAPS	TMS
6	MAPS	DDA
7	MAPS	SDS
8	MAPS	PLU

Adsorption Methodology

Batch Tests

The maximum adsorption capacity of bridged silsesquioxanes (BSSOs) was determined by the adsorption of PFOA and PFOS from concentrated solutions. The adsorption study was performed by placing 0.2 g of obtained adsorbents **1-8** in 50 mL of 0.5 % PFOA or PFOS solutions. The mixture was left stirring at room temperature for 16 h. After adsorption, the solid phase was filtered, washed with deionized water until pH = 7, and dried on air. Contents of PFOS and PFOA in the samples were calculated from the contents of total fluorine.

Adsorption Isotherms

0.1 g of adsorbent **1** and **5** were mixed with 10 mL of PFOA and PFOS solutions of four different concentrations: 100, 200, 300, and 400 mg/L. The mixture was kept for 2 h at constant temperature (21, 30, and 40°C) in a circulating water bath (Thermo Scientific, Pittsburg, PA).

Equilibrium concentrations of PFCs on the adsorbent (q_e) and in the solution (C_e) were determined from analysis of the adsorbents on total fluorine.

Column Tests

Column tests were performed using PFOA and PFOS solutions with concentrations of 100, 200, 300, and 400 mg/L. The adsorbents were granulated by tableting the powder samples at a pressure of 9 metric tons and separating the 1–2 mm fraction on Fisher Scientific test sieves. The solutions passed through a column with an internal diameter of 5 mm containing 0.5 g of granulated adsorbent **1** and **5** mixed with glass beads. The flow rate of 3 mL/(g•min) was maintained by Carter Manostat peristaltic pump (Cole-Parmer, Vernon Hills, IL). For determination of the effect of flow rate on the adsorbent effectiveness, different amount of the adsorbents (0.1-0.5 g) were taken, that corresponded to flow rates 6-30 mL/(g•min). Eluate samples were collected every 2 min and analyzed using ^{19}F NMR.

Regeneration

Regeneration of samples containing adsorbed PFCs was conducted in a 5% solution of KOH in CH_3OH . A sample (0.1 g) was mixed with 10 mL of the solution and left on a shaker for 20 h. Then it was filtered, washed by DI water and acetone, and dried on air. The remaining amount of PFCs was determined by analysis of total fluorine.

Instrumental Analysis and Characterization

Elemental Analysis

The elemental analysis performed on total organic C, H, N and F was provided by Robertson Microlit Laboratories (Ledgewood, NJ).

¹⁹F NMR Spectroscopy

¹⁹F NMR spectra of the solutions were recorded on a JNM-ECZS 400 FT NMR spectrometer (JEOL USA, Peabody, MA) at 400 MHz in D₂O as a solvent. The number of scans was 140 at pulse length of 6.35 μs and delay time of 4 s. Concentrations of dissolved PFCs were calculated from relative intensity of CF₃ peaks of TFMSA (−78.6 ppm) and PFOS or PFOA (−80.6 ppm).

FT-IR Spectra

FT-IR spectra were recorded in KBr pellets on a Genesis II spectrometer (Shimadzu, Kyoto, Japan).

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

DSC and TGA analyses were provided by Robertson Microлит Laboratories. The DSC curve was recorded on a Pyris Diamond differential scanning calorimeter (Perkin Elmer, Waltham, MS) in a sealed pan. TGA analysis was conducted on a Perkin Elmer TGA 7 analyzer. The heating rate was 10 °C/min.

Particle Sizes

Particle sizes were determined by dynamic light scattering on a Zetasizer Nano ZS90 (Malvern, UK). The samples were dispersed in water for 10 min at sonication prior to analysis.

Brunauer-Emmett-Teller (BET) Surface Areas

BET surface areas were measured on a Quantachrome Nova 2200e porosimeter (Boynton Beach, FL). Prior to measurements, the samples were degassed at 150 °C in vacuum for 2 h. Adsorption/desorption isotherms were recorded at -196 °C using N₂ as an adsorbate. The BET

surface areas were calculated from the adsorption branch of isotherms to be in the range of $P/P_0 = 0.1-0.3$.

TEM Imaging

TEM study was conducted on a JEOL 2100F transmission electron microscope (JEOL USA, Peabody, MA) at 200 keV operated in scanning mode (STEM) at spot size of 0.2 nm. Images were collected with JEOL annular dark field detector and Gatan bright field detector. A sample was dispersed in ethanol and sonicated for 10 minutes. Then 5 drops of 0.5% RuO₄ solution were added and a dispersion was stirred for 2 minutes. One drop of this dispersion was added to formvar coated 200 mesh Cu TEM grid, left for 20 seconds and the residual was wicked away. The grid was washed by a drop of ethanol.

CHAPTER 3. RESULTS

Synthesis of BSSOs

Formation of the gel after 20% HCl, and the respective precursors were simultaneously added dropwise to the solutions of various surfactants. Samples **4** and **8** were prepared using a non-ionic surfactant, Pluronic P123. Ionic surfactants were used for the preparation of the rest of the samples. Samples were prepared using the precursor TMPA gave a high yield of products ranging from 0.78-0.93 g/g_{pr}. The sample that gave the highest yield was **3** (0.93 g/g_{pr}). Samples prepared using MAPS as the precursor also gave good yield ranging from 0.61-0.81 g/g_{pr}. The contents of amino groups (potential adsorption sites) in the materials were almost similar (Table 5). The ratio C/N was some less than in the precursors except for samples **3** and **7**. The materials were highly hydrophilic. The content of amino groups in all the samples were similar, ranging from 3.1-3.5 mmol/g. The loading of amino groups in the samples ranged from 10.2-97.9 molecules/nm².

Adsorption of PFCs

Batch Tests

The adsorption capacities of the various adsorbents on PFOA and PFOS were recorded in gram per 100 g of adsorbent. All the samples showed incredible adsorption capacities in the adsorption of both PFOA and PFOS of 0.5 % concentration. The surfactant used for the synthesis of adsorbent with the best adsorption of both PFOA and PFOS was TMS. Hence the sample **1** and **5** were used in the subsequent research. Sample **7** adsorbed the highest amount of PFOS of approximately 90% on its surface (Fig. 9).

Table 5. Results of Elemental Composition, Yield, the Content of Amino Groups and Loading of Amino Groups of Samples **1-8**

Sample	Elemental composition of the organic phase	Yield (g/g _{pr.})	Content of amino groups, mmol/g	Loading of amino groups, molecules/ nm ²
1	C _{5.5} H _{18.3} N	0.83	3.2	10.2
2	C _{5.8} H _{17.9} N	0.86	3.5	38.9
3	C _{6.6} H _{18.3} N	0.93	3.2	15.0
4	C _{5.3} H _{18.8} N	0.78	3.4	28.7
5	C _{6.7} H _{20.6} N	0.76	3.2	46.8
6	C ₆ H _{20.9} N	0.61	3.2	68.1
7	C _{7.3} H _{20.2} N	0.81	3.3	16.9
8	C _{6.2} H _{18.1} N	0.72	3.1	97.9

Most of BSSOs demonstrated an excellent capability of PFCs removal from water. Samples **1-4** obtained from TMPA had lower adsorption capacity (198-466 mg/g) than samples **5-7** obtained from MAPS (260-868 mg/g). However, the sample **8** had the lowest adsorption capacity and this may be due to the non-ionic surfactant used. Adsorption of PFOA on all samples was higher than PFOS except sample **7**, for which adsorbed 1.8 mmol/g PFOS or 86.8% of the adsorbent weight.

After the adsorption, all materials became highly hydrophobic and floated on the surface of the water. All the synthesized material placed in water (Fig. 10a) resulted in the formation of a cloudy solution because of the solvation of the solid. However, after the adsorption, the synthesized material appeared completely hydrophobic (Fig. 10b). Such a drastic change in adsorbent hydrophilicity was observed for all eight samples.

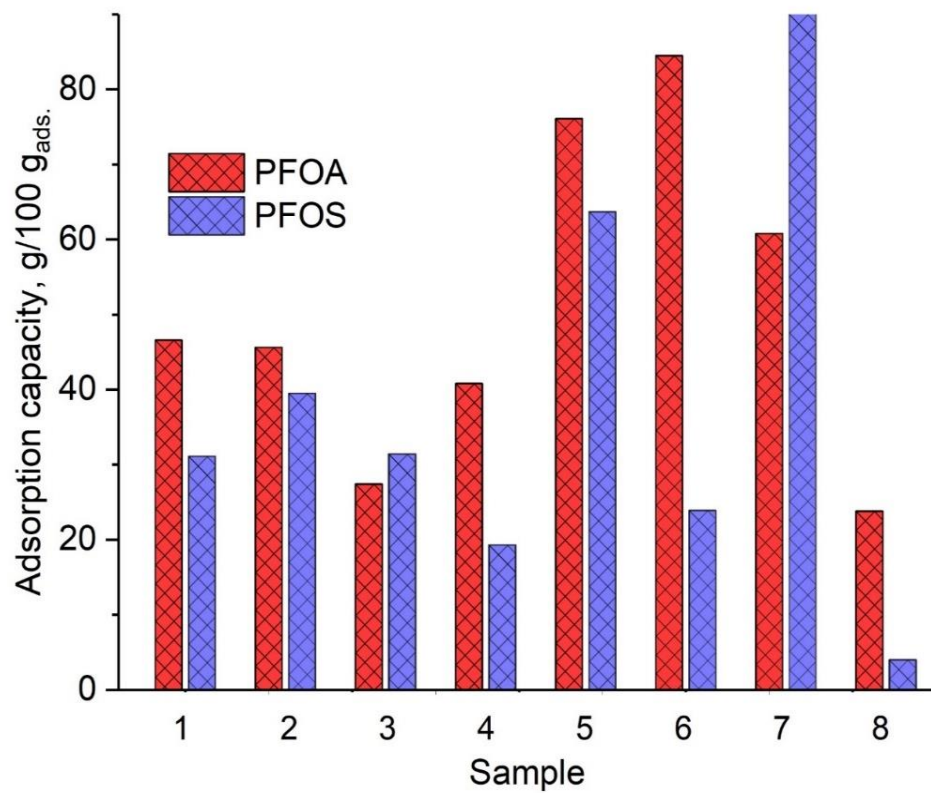


Figure 9. Adsorption of PFOA and PFOS by various adsorbents

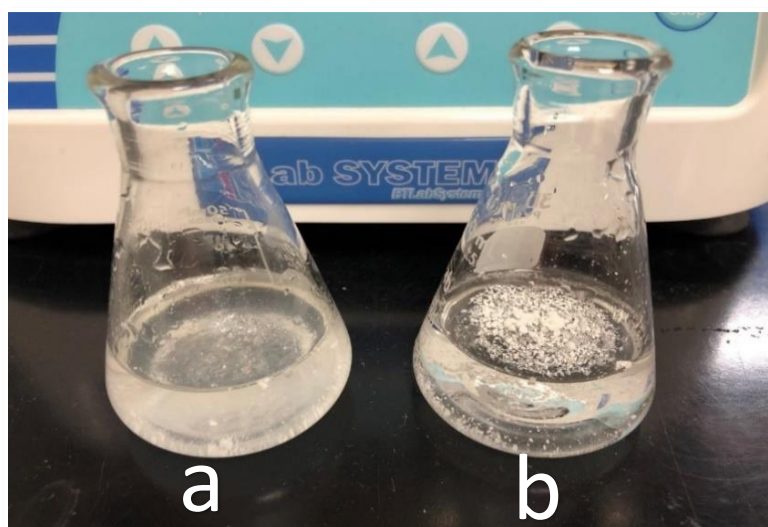


Figure 10. The synthesized adsorbent in water before (a) and after (b) adsorption of PFOA

Regeneration

Treatment of samples **1** and **5** with PFCs on their surfaces by methanol solution of KOH resulted in the elimination of 96-99% of PFCs. As shown in Fig 11., sample **5** with PFOA gave the best regeneration result. The content of PFOA on its surface had decreased from 750 to 10 mg/g_{ads} after regeneration. Sample **5** with PFOS gave PFOS content of about 20 mg/g_{ads} after regeneration.

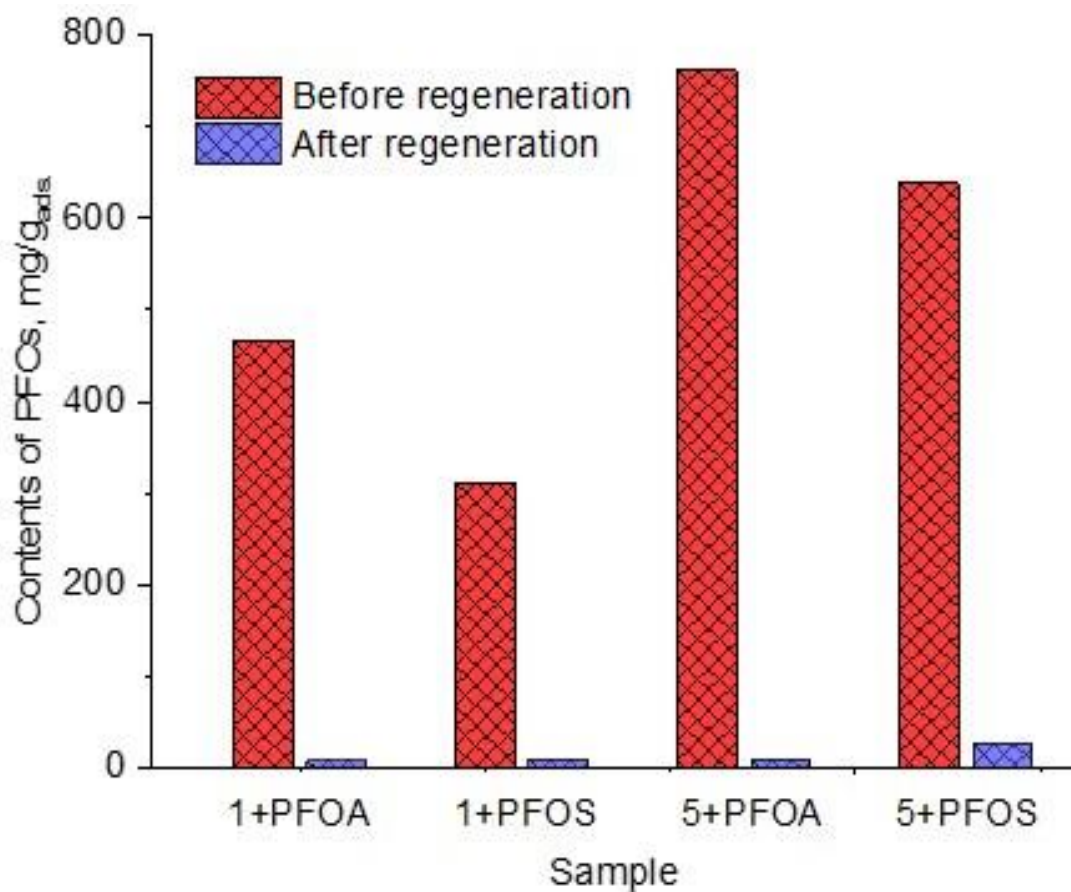


Figure 11. Regeneration of samples **1** and **5** containing adsorbed PFCs

Adsorption Isotherms

Isotherms of adsorption of PFCs on materials **1** and **5** do not fit the Langmuir model. Adsorption of PFOA on both samples well fits the Freundlich model $q_e = K_F C_e^{1/n}$ with R^2 between 0.957 and 0.996 (Fig.12). In contrast, the adsorption of PFOS fits the Freundlich model only for sample **5** ($R^2 = 0.99$). In the case of sample **1**, isotherms have the shape of BET type with an increase of adsorption at higher concentrations of PFOS.

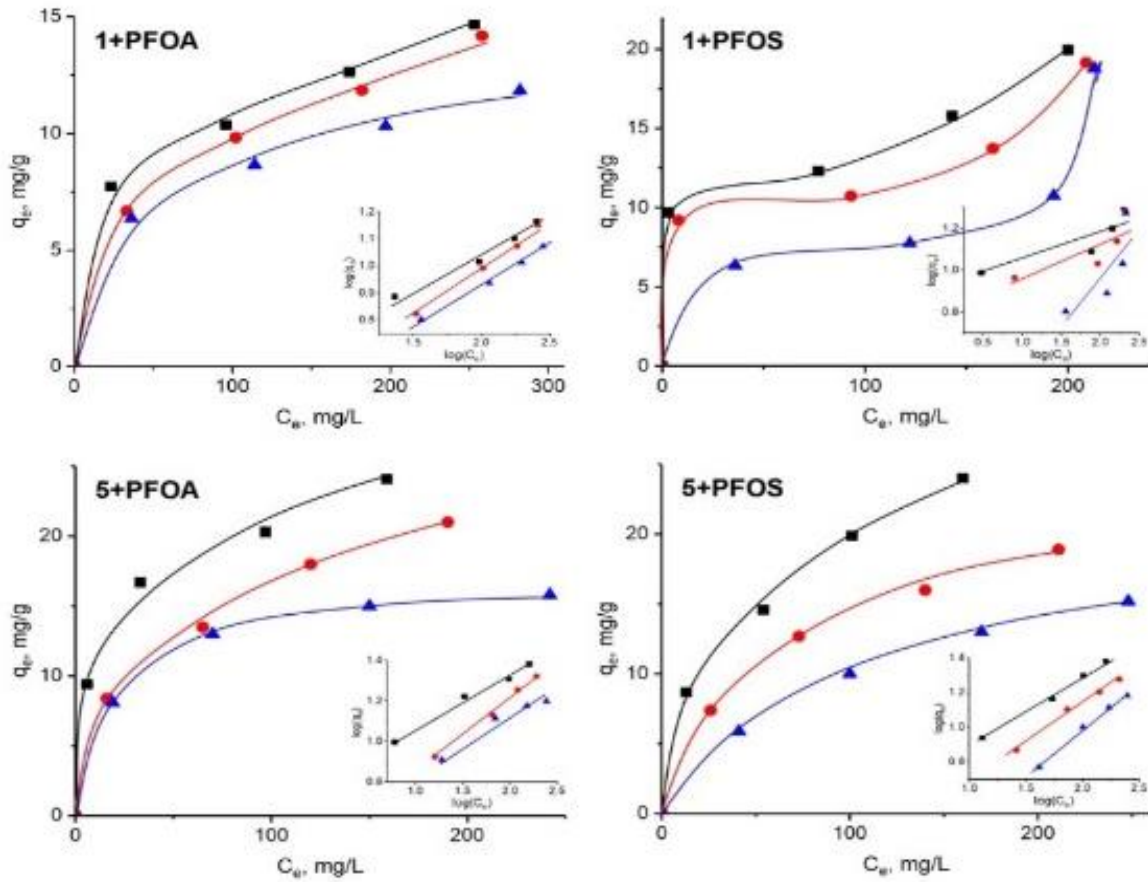


Figure 12. Isotherms of adsorption of PFOA and PFOS on materials **1** and **5** and linear fitting plots of Freundlich isotherm models at different temperatures ($^{\circ}\text{C}$): 21 (\blacksquare), 30 (\bullet), and 40 (\blacktriangle)

Column tests

Column tests confirmed the high effectiveness of the adsorbents in the removal of dissolved PFCs even at high concentrations. In most of the water samples, after adsorption, the remaining level of concentrations of PFCs were below the detection limit of NMR spectroscopic analysis (5 ppm). The only exception was the adsorption of PFOA on TMPA-derived material, where notable amounts of the contaminant were detected in the eluents (Fig. 13).

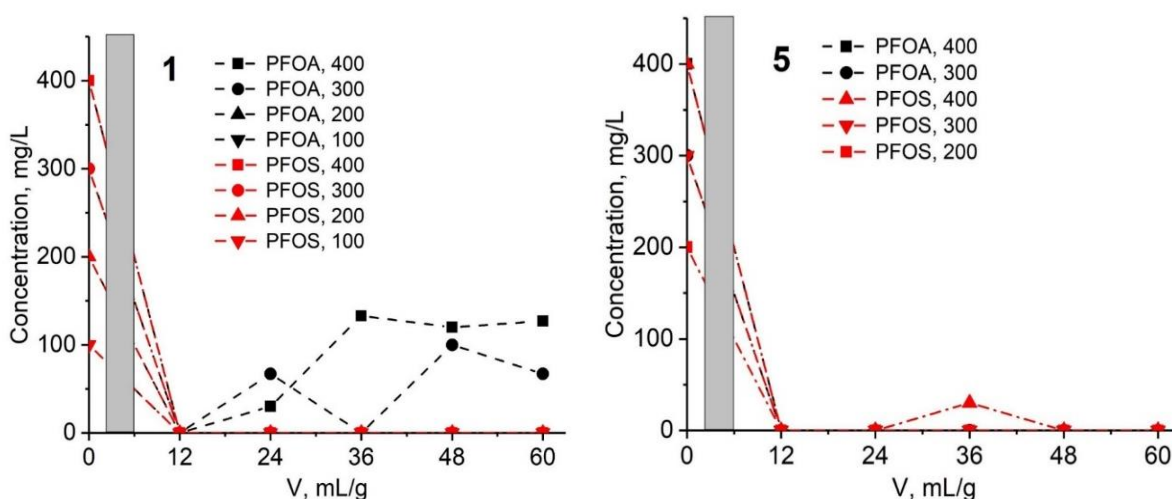


Figure 13. Column tests on samples 1 and 5

Flow Rate

The study of the effect of flow rate showed a clear difference between TMPA- and MAPS-derived adsorbents (Fig. 14). The sample 1 was useful only at a low flow rate not exceeding 6-8 mL/(g•min). At higher flow rates, a significant part of the PFCs passed through the adsorbent without interaction. In contrast, sample 5 demonstrated the effectiveness of up to 20 mL/(g•min).

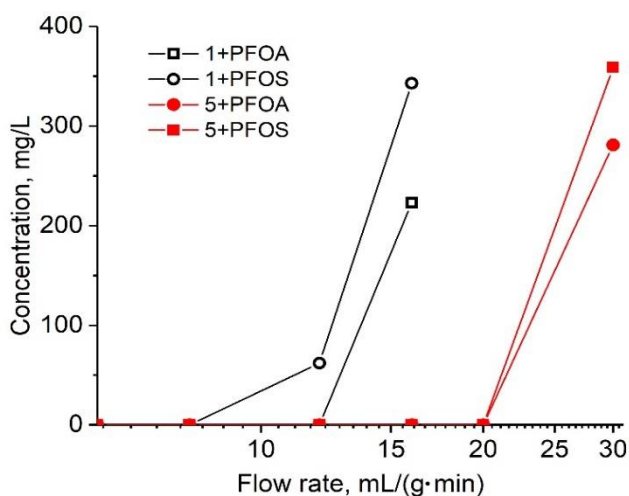


Figure 14. Effect of flow rate on the adsorption of PFOA and PFOS

FT-IR Spectra Analysis

FT-IR spectra of the synthesized BSSOs (Fig. 15) showed spectra of samples **1** and **5** contain absorption bands characteristic for silica gel and an organic phase. Vibrations of the silica network produced bands at 458 (δ_{SiOSi}), 1055 (ν_{SiOSi}) and 1130 cm^{-1} (ν_{asSiOSi}). Bands at 910 (ν_{SiO}), 1636–1652 (δ_{HOH}), and 3433 cm^{-1} (ν_{OH}) are attributed to the silanol groups. The presence of the organic phase is evident from bands at 1473 (δ_{CH_2}) and 2804–2957 cm^{-1} (ν_{CH_2} , two bands). In addition, a strong band at 694 cm^{-1} indicates ν_{SiC} vibrations. Spectra of samples 2-4 and 6-8 were similar as compared to **1** and **5**, respectively.

The presence of adsorbed PFOA and PFOS in the materials after adsorption was evident from characteristic absorption bands of polyfluoroalkyl groups. These bands are located at 1211 and 1247 cm^{-1} (ν_{CF}) in Fig. 16 for the FT-IR spectra of PFOA.

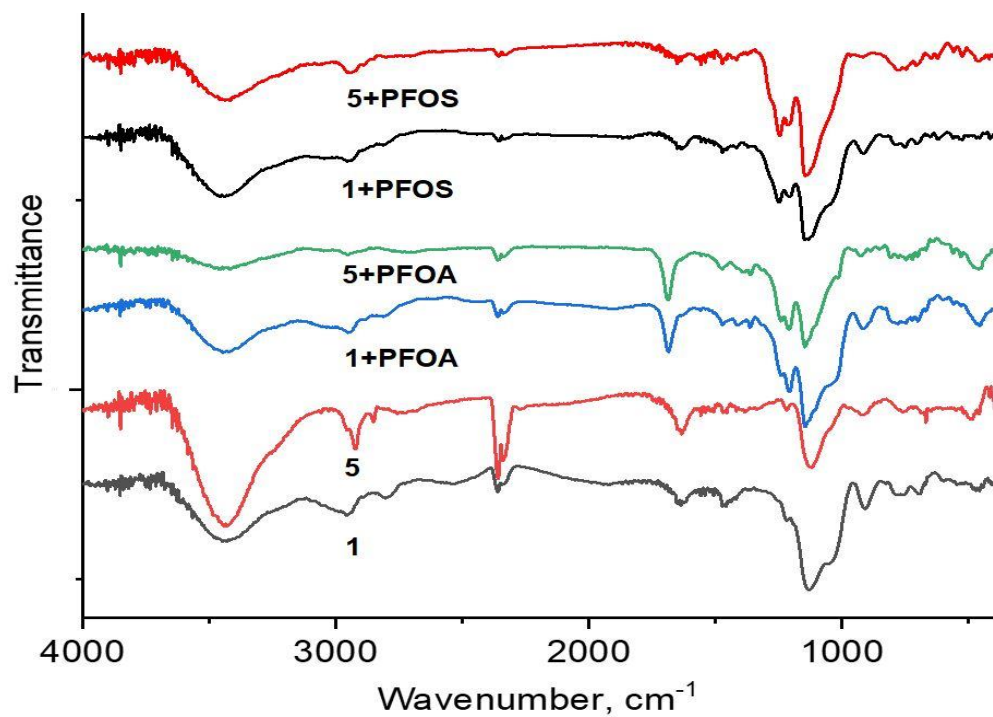


Figure 15. FT-IR spectra of **1** and **5** before and after adsorption

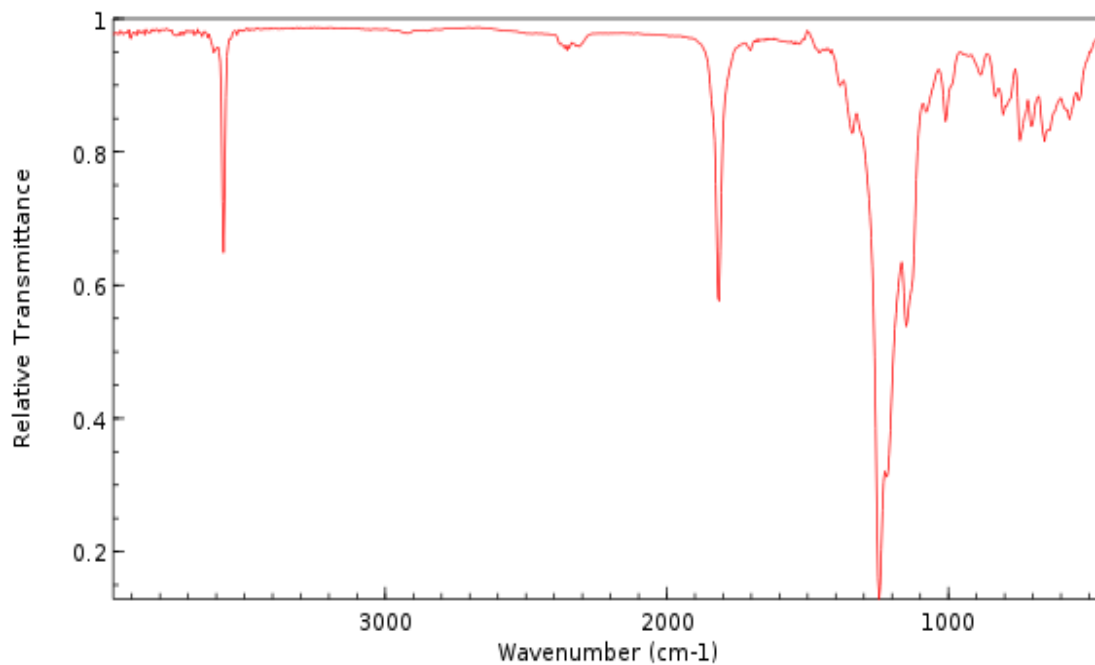


Figure 16. FT-IR spectra of PFOA

Thermoanalysis

Differential scanning calorimetry (DSC) is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. DSC spectrum of sample **1** demonstrated its stability up to 172 °C (Fig. 17). In this range, physically adsorbed water (10 % by weight) desorbed, mostly below 100 °C. Heating above 172 °C leads to its degradation, which occurred in three steps: 172-222, 222-400, and 400-700 °C, with a total weight loss of 40%. The same sample with adsorbed PFOA had mostly similar behavior. However, the fast desorption of PFOA from the material co-occurred with its degradation. The TGA curve of this sample has an additional sharp step in the range of 180-220 °C, with a weight loss of 31 %.

Dynamic Light Scattering

Particle sizes of the adsorbents varied in the full range from 13 to 301 nm (Table 6). Particle size distributions of each adsorbent were mostly narrow. For example, all particles of sample **1** were between 80 and 100 nm in diameter (Fig. 18). Adsorption of PFCs strongly favored agglomeration of the particles up to 732 nm.

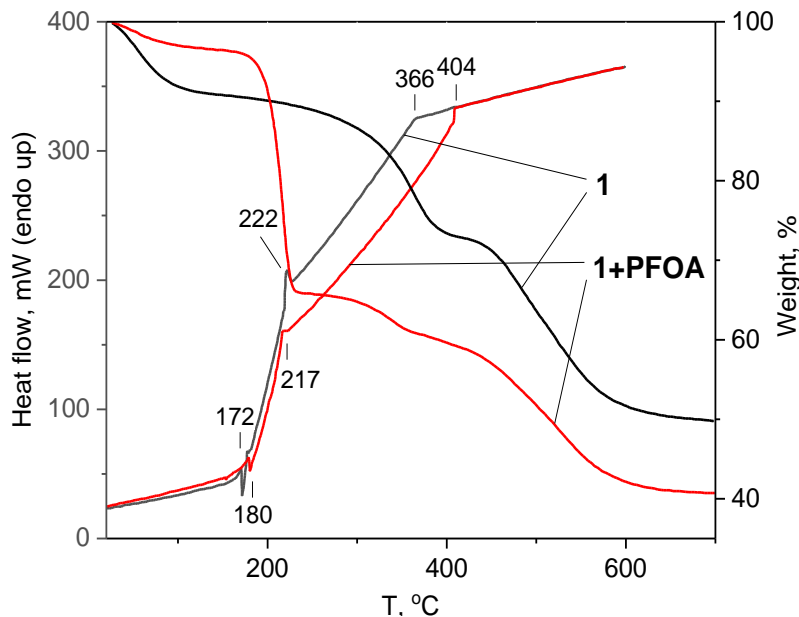


Figure 17. DCS and TGA curves of sample **1** before and after adsorption of PFOA

Table 6. The Particle Size Distribution of Samples **1-8** Before and After Adsorption of PFOA/PFOS

Sample	Precursor	Surfactants	Particle Size, nm		
			Before	After (PFOA)	After (PFOS)
1	TMPA	TMA	91	118	361
2	TMPA	DDA	157	266	190
3	TMPA	DDS	66	91	244
4	TMPA	Pluronic P123	301	313	732
5	MAPS	TMA	142	164	269
6	MAPS	DDA	13	38	190
7	MAPS	DDS	59	115	368
8	MAPS	Pluronic P123	68	151	295

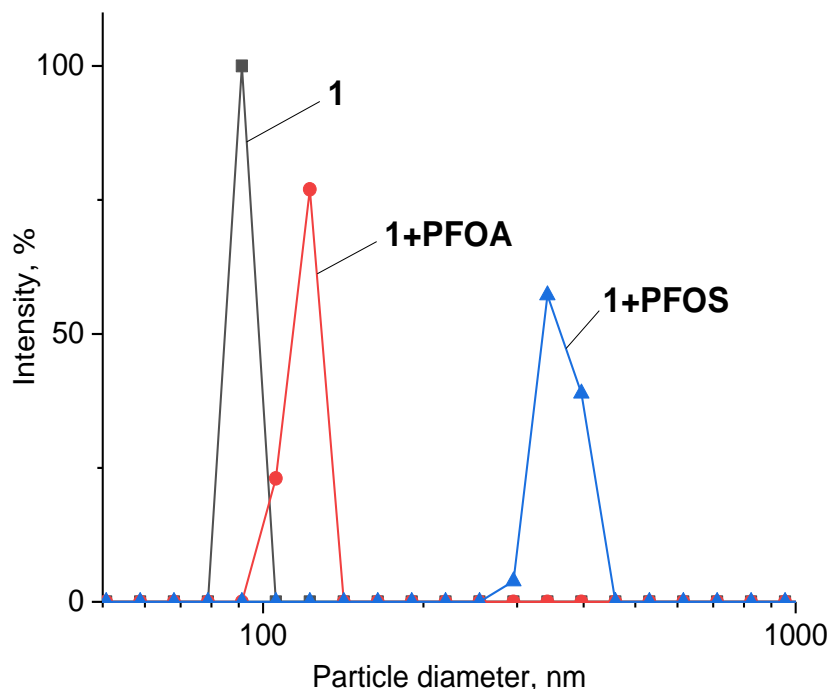


Figure 18. Particle size distribution in sample **1** before and after adsorption

Porosimetry

All obtained BSSOs were mesoporous with BET surface areas 18.7-189.4 m²/g (Table 7). The surface loading of amino groups depended on the BET surface area and varied between 10.2 and 97.9 molecules per nm². Adsorption of PFCs reduced the BET surface area of all samples to 2.1-87.0 m²/g. The most significant reduction was observed for samples with the highest loading of the adsorption sites.

TEM Imaging

TEM images of samples **1** and **5** showed that they are formed by large, highly branched agglomerates of particles of about 100 nm in diameter (Fig. 19). The sizes of these agglomerates exceed 1 μm. The images confirmed the mesoporous structure of the particles with pore sizes of about 2-4 nm. No notable difference between the structures of these materials was detected.

Table 7. BET Surface Area of Samples **1-8** Before and After Adsorption of PFOA and PFOS

Sample	Precursor	Surfactants	BET Surface Area, m ² /g		
			Before	After (PFOA)	After (PFOS)
1	TMPA	TMA	189.4	52.6	56.6
2	TMPA	DDA	54.5	17.0	12.9
3	TMPA	DDS	128.2	43.1	81.9
4	TMPA	Pluronic P123	71.2	54.7	38.0
5	MAPS	TMA	40.9	26.6	7.0
6	MAPS	DDA	28.2	2.1	17.3
7	MAPS	DDS	117.2	87.0	78.3
8	MAPS	Pluronic P123	18.7	8.2	14.9

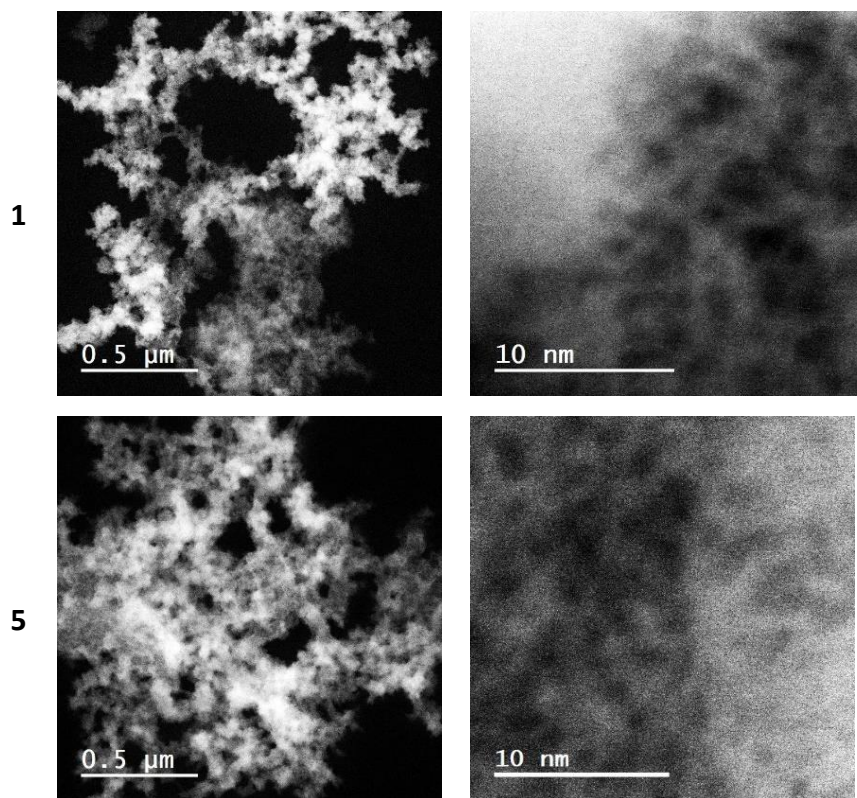


Figure 19. TEM Imaging for sample **1** and **5**

CHAPTER 4. DISCUSSION

High yields of the products which were obtained proved complete polycondensation of TMPA and MAPS to corresponding BSSOs. The prepared mesoporous materials were highly hydrophilic and absorbed water up to 10 % by weight. The contents of amino groups in all materials were almost similar. Their slightly increased content in sample **2** might be caused by a small amount of entrapped DDA.

High contents of primary adsorption sites in the adsorbents provides the high adsorption capacity for PFCs. This value varied between 0.5 and 2.2 mmol/g for different combinations of adsorbents and adsorbates. The concentration of amino groups in the materials were 3.1-3.5 mmol/g, and this shows that only part of adsorption sites interacted with the PFCs. This is because, after PFCs adsorption, concentrations of amino groups were still recorded on the surfaces of the materials. Their incomplete involvement was caused by inaccessibility of some adsorption sites due to steric hindrances. The adsorption occurred by a multilayer mechanism through not only ionic interaction between acidic groups of PFCs and significant groups such as oxide on the surface of BSSOs. Hydrophobic interaction between PFC molecules and surfaces of BSSOs makes another contribution to the adsorption of these PFCs.

Strong bonding of PFCs to the BSSO surface is evident from the thermal stability of adsorbed species. The thermal behavior of BSSOs was similar to non-bridged ones. At 172 °C, powder material **1** converted to glassy solid with no weight loss. The decomposition started at 221 °C and occurred in two steps. On the first step, up to 400 °C weight loss was 17%. Between 400 and 700 °C, the material lost 23% of its weight. These results corresponded to the total elimination of the organic phase, hence transformation to silicon oxide. All these transformations also occurred with PFC-containing samples and an additional step that was observed on PFC

elimination was at 180-220 °C. Thus, the desorption of adsorbed substance occurred on the step of glass transition before the thermal decomposition of the adsorbent. The elimination of PFC was due to the loss of the adsorbent porosity after the glass transition temperature.

Adsorption of PFCs makes significant changes to the porosity and particle size of BSSOs. In all experiments of all the samples, the BET surface area decreased after PFCs adsorption. This change is caused by the adsorbate molecules blocking the pores on the surfaces of BSSOs and particle agglomeration. No direct correlation between the BET surface area of an adsorbent and its adsorption capacity was found. Moreover, materials with lower surface area in most cases adsorb higher amounts of PFCs. It confirmed the multilayer adsorption mechanism on the surface.

Polyfluorinated alkyl groups of PFCs are highly hydrophobic. After adsorption, they changed particle surfaces from hydrophilic to hydrophobic. It then further caused hydrophobic agglomeration of the particles in water solution. This effect was also responsible for the loss of wettability of the samples that caused the flotation of used adsorbents in aqueous media. Higher hydrophobicity resulted in a better agglomeration degree. Since PFOS is more hydrophobic than PFOA, PFOS caused a higher agglomeration degree than PFOA (Table 7).

Interestingly, BSSOs synthesized from MAPS showed better adsorption capacity than materials obtained from TMPA. This trend is unusual because secondary amines are more effective in adsorption of the acidic molecules. However, non-electrostatic hydrophobic interaction between the adsorbent surface and perfluorinated tail of the adsorbed molecules plays a significant role in the mechanism of adsorption. MAPS, as a tertiary amine, produces more hydrophobic BSSOs than TMPA.

The differences between TMPA and MAPS were more obvious from the corresponding column adsorption tests of PFCs on samples **1** and **5**. Due to the higher basicity of TMPA (calculated $pK_a = 10.78$), the adsorption of PFOA on this material is lower compared to the adsorption of PFOS (Fig.12). It should be noted that the adsorption rate was fast at the beginning of the process and then slowed down later. For example, at a flow rate of 6 mL/g, after 10 min, sample **1** adsorbed only 19 mg/g of PFOA that corresponded to 79% of its full amount. In the case of PFOS, it adsorbed 24 mg/g or 100%. It can be explained by the high accessibility of adsorption sites located on the external surface of the particles and diffusion limitations inside the pores. In contrast with TMPA, MAPS with lower basicity ($pK_a = 9.76$), meaning more hydrophobic due to its inability to react with water, demonstrated higher adsorption of PFCs. Since hydrophobic groups enhance PFCs adsorption. PFOS, as a strong acid, readily adsorbed on both materials. Hence Sample **5** which is a product of MAPS showing almost complete adsorption of both PFOA and PFOS.

The study of the effect of flow rate on both adsorbents also confirmed higher effectiveness of sample **5**, a product of MAPS. It maintained excellent adsorption ability up to 20 mL/(g•min), while sample **1**, a product of TMPA became ineffective already at 6 mL/(g•min). The reason is that the available adsorption sites in the adsorbent synthesized from MAPS were higher than TMPA due to lower diffusion limitations.

Isotherms of adsorption of PFOA on samples **1** and **5** and PFOS on sample **5** did not fit the Langmuir model for monolayers on homogeneous surfaces. Moreover, they suitably fit the Freundlich model that indicates heterogeneity of the adsorbent surface. The shape of adsorption isotherms of PFOS on sample **1** implies a more complicated mechanism of its adsorption that involves multilayer. PFOS is a significantly stronger acid than PFOA. While pK_a of PFOS is -

3.27, it is only 2.8 for PFOA. This difference also shows the comparative adsorption of PFOA and PFOS on ordinary silica gel. In this case, the adsorption capacity on PFOS is 33.3 times higher than on PFOA. Considering the weak ability of silica gel to protonation, surface silanol groups or bridge oxygen atoms of BSSOs cannot be protonated by PFOA in a notable degree; however, strong PFOS can protonate them. This is because PFOS is a Pearson hard base and will react with the hard acid surface of BSSOs (silanol groups). Therefore, the adsorption of PFOS in this case, might occur not only on amino groups but also on structural oxygen atoms.

Conclusions

The bridged amino-functionalized trimethoxysilanes in acidic media with the surfactants provided the stable mesoporous silsesquioxanes. The obtained materials with high contents of accessible primary sites demonstrated excellent adsorption capacity for PFOA and PFOS. Especially efficient adsorbents synthesized from bis[3-(methylamino)propyl]trimethoxysilane adsorbed up to 86.8% of a PFC by weight. Because of the electrostatic attraction between carboxylate/sulfonate ions and protonated amino groups, and the hydrophobic interaction between the polyfluorinated chain and surface alkyl groups, a high adsorption capacity for PFCs is attained. The materials are thermally stable in the range of temperatures expected use. Although PFC solutions studied in this work had higher concentrations than in natural water sources, the excellent performance of the adsorbents makes them promising materials for potential applications in filters for drinking water.

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VITA

BERTHA LOTSI

- Education: M.S. Chemistry, East Tennessee State University,
Johnson City, Tennessee, 2020
- B.S. Chemistry, Kwame Nkrumah University of
Science and Technology, Kumasi, Ghana. 2014
- Professional Experience: Physiochemical Analyst, Ghana Atomic Energy
Commission, Ghana, 2014-2015
- Assistant Equipment Controller, Queiroz Galvao
Construction, Accra, Ghana, 2016-2018
- Teaching Assistant, East Tennessee State University,
College of Arts and Science, 2018-2020
- Publications: Vigbedor, B. Y.; Osafo A. S.; Gyan B. A.; Lotsi B.
In vitro Antimalarial Activity of the Ethanol Extracts of
Azelia africana and *Cassia alata* commonly used as Herbal
Remedies for Malaria in Ghana. *Inter. J. Novel. Res. Life Sci.*
2015, 10-16
- Presentations: 1. **Lotsi B**, Kuvayskaya A, Mohseni R, Vasiliev A. Mesoporous
Adsorbent for Per-fluorinated Compounds. *15th Annual P3 Awards:
A National Student Design Competition Focusing on People,
Prosperity and the Planet, FON EPA-G2018-P3-Q2*. Boston,
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