

A ‘Concentrate-&-Degrade’ Technology for Cost-Effective Adsorption and Photodegradation of Per-and Polyfluoroalkyl Substances in Municipal Landfill Leachate

by

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that have been widely used in industry and daily consumer products. Due to the wide application of these products and their recalcitrant nature to conventional degradation procedures, these chemicals have been widely found in the environment including water, wastewater, and landfill leachate, which poses various adverse health effects. Because municipal landfill has served as the endpoint of many PFAS-laden materials, high concentrations of PFAS have been detected in landfill leachate. As the PFAS-related regulations are rapidly evolving in recent years, it is critical to reduce the PFAS concentrations in landfill leachate before it is transferred to wastewater treatment plants. However, there has been no cost-effective destructive technology available for the degradation of PFAS in landfill leachate.

In this regard, we have developed and tested a two-step “concentrate-&-destroy technology” for the treatment of PFAS. The key for the technology was a new type of adsorptive photocatalyst referred to as Bi/TNTs@AC. Using perfluorooctanoic acid (PFOA), one of the most widely detected PFAS in landfill leachate, as a model compound, we tested the material with respect to both adsorption and the subsequent photodegradation of PFAS under real-world landfill leachate matrix conditions. The specific objectives were to: 1) Prepare the material based on commercially available activated carbon (AC) and TiO₂ and under alkaline hydrothermal conditions, 2) Measure the adsorption capacity and kinetics of PFOA, 3) Test the subsequent solid-phase photodegradation of PFOA under UV irradiation (wavelength = 254 nm, intensity = 210 W/m²), 4) Explore ways to enhance the photodegradation effectiveness (pH, temperature, oxidants, and of Fe³⁺), and 5) Examine the reusability of the materials without invoking chemical regeneration.

Batch experimental data indicated that Bi/TNTs@AC at a dosage of 5 g/L was able to adsorb more than 75% of PFOA (initial concentration = 100.947 $\mu\text{g/L}$) within 1 hour despite the strong matrix effect of landfill leachate. The adsorption equilibrium was achieved in 24 h, with >95 % of PFOA adsorbed. After the adsorption, the solid was subjected to UV irradiation (wavelength = 254 nm UV intensity = 210 W/m^2 and irradiation time = 4 h) at a pH of 9.43. As a result, >46% of pre-adsorbed PFOA was defluorinated (i.e., conversion of fluorine in PFOA into fluoride) in 4 h. The addition of Fe^{3+} (60 μM) during the photodegradation increased the defluorination rate by 58 %. Furthermore, elevating the reactor temperature from 38 $^{\circ}\text{C}$ to 63 $^{\circ}\text{C}$ and addition of persulfate (100 μM) increased the defluorination from 46% to 55.4% and 54%, respectively. The technology appeared promising for cost-effective treatment of PFAS in landfill leachate.

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List of Abbreviations

Bi	Bismuth
DOM	Dissolved organic matter
FeCl ₃	Ferric chloride
GAC	Granular activated carbon
HDPE	High density polypropylene
K ₂ S ₂ O ₈	Potassium per sulfate
NaOH	Sodium hydroxide
NF	Nano-filtration
POPs	Persistent organic pollutants
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonic acid
PFPeA	Perfluorophosphonic acid
PFPeS	Perfluoropolyethers
PFH _x A	Perfluorohexanoic acid
PFH _x S	Perfluorohexane sulfonate
4:2 FTS	4:2 Fluorotelomer sulfonic acid
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptanesulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate

6:2 FTS	6:2 Fluorotelomer sulfonic acid
PFOSA	Perfluorooctanesulfonamide
PFNA	Perfluorononanoic acid
PFNS	Perfluorononanesulfonic acid
PFDA	Perfluorodecanoic acid
PFDS	Perfluorodecanesulfonic acid
8:2 FTS	8:2 Fluorotelomer sulfonic acid
PFUnA	Perfluoroundecanoic acid
MeFOSAA	N-Methylperfluorooctane sulfonamidoacetic acid
PFDoA	Perfluorododecanoic acid
EtFOSAA	N-ethyl-perfluorooctane sulfonamido acetic acid
PFTTrDA	Perfluorotridecanoic acid
PFTeDA	Perfluorotetradecanoic acid
SPE	Solid phase extraction
TNT	Titanate nanotubes
TiO ₂	Titanium dioxide
TDS	Total dissolved solids
USEPA	United States Environmental Protection Agency

Chapter 1. General Introduction

1.1: Background

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals containing stable C–F bond with bond energy of (536 kJ mol^{-1}) (Li et al., 2021; Shahsavari et al., 2021; Singh et al., 2019; Wei et al., 2019). The PFAS have been widely produced since the 1940's and utilized for numerous industrial and domestic applications, such as daily based household products, fluoropolymers surfactants, aqueous film-forming foams, metal plating, textiles, etc. (Ahrens & Bundschuh, 2014; Wei et al., 2019). Due to their widespread application and highly resistant to degradation these chemicals have been found in the environment, directly associated with adverse health effects (Hu et al., 2016; Li et al., 2020). Since the final destination of most PFAS are landfills, it leaches to the leachate and can contaminate the soil and water bodies (Tian et al., 2021). Previous studies indicate that between the years 2009 to 2017 around 455 PFAS have been detected in aquatic environments in which Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are the most dominant PFAS in drinking water (Tian et al., 2021; Wei et al., 2019; Xiao., 2017).

According to previous research reports, landfill leachate is considered a significant secondary source of PFAS contamination, in 2013 around 563 to 638 kg of PFAS from landfill leachate were discharged to wastewater treatment plants in the USA (Lang et al., 2017). The most dominant PFAS present in landfill leachate in the USA, as reported by Lang et al (2017), are 5:3 fluorotelomer carboxylic acid (5:3 FTCA), perfluorohexanoic acid (PFHxA), perfluorobutanoic acid (PFBA), PFOA, 6:2 fluorotelomer carboxylic acid (6:2 FTCA), and perfluoropentanoic acid (PFPeA). It is mentionable that landfill leachate is treated in municipal wastewater treatment plants

where PFAS are poorly or partially treated or removed (Benskin et al., 2012). Therefore, management and treatment of landfill leachate are highly required before discharging it into natural water bodies for preventing the potential PFAS release to adjacent water bodies and wastewater treatment plants (Masoner et al., 2020)

Due to the widespread application of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) for commercial and industrial purposes, they are considered the most encountered PFAS (Singh et al., 2019). Human exposure to PFAS is associated with cancer, elevated cholesterol, obesity, immune suppression, and endocrine disruption (Hu et al., 2016). According to Hu et al, (2016) the drinking water supplies of 6 million US citizens is more than 70 ng/L for PFOA and PFOS which exceed US EPA's advisory level for drinking water (Hu et al., 2016). Therefore, the PFAS removal from the environment has been prioritized , for example the United States Environmental Protection Agency (USEPA) in the early 2000's wanted 3M company to reduce the production of PFOA and related derivatives (Wei et al., 2019), moreover, EPA has established a health advisory level (HAL) of 70 ng/L for combined concentration of PFOA and PFOS in 2016 for drinking water (EPA, 2016; Maldonado et al., 2021). This health advisory level has been updated and reduced to 0.004 ng/L and 0.02 ng/L for PFOA and PFOS, respectively in June 2022 (Cousins et al., 2022; Zenobio et al., 2022 ; US EPA 2022).

Several technologies have been proposed and employed for the removal and degradation of PFAS from water. PFOA was effectively removed by adsorption using activated carbon, (Li et al., 2020; Zhang et al., 2016), ion exchange resin (Wang et al., 2019), anionic exchange, metal-organic framework (Liu et al., 2015), activated carbon fibers (Wang et al., 2015), carbon nanotubes (Deng et al., 2012), and starch-stabilized magnetic nanoparticles (Gong et al., 2016). Treatment technologies such as adsorption with granular activated carbon (GAC), membrane nano-filtration

(NF), and reverse osmosis (RO) have also been proposed for the treatment and removal of PFAS from drinking water (Maldonado et al., 2022). These proposed technologies possess certain disadvantages such as, unable to degrade PFAS, adsorbent regeneration requires expensive organic compounds and toxic solvent such as methanol and ethanol, and regeneration of materials requires additional cost for disposal (Deng et al., 2015; Du et al., 2015; Li et al., 2020).

Due to the high concentration of total organic carbon (100 – 10,000 mg/L) and dissolved/suspended solids, leachate is a highly electrically conducting solution (Gallen et al., 2017; Singh et al., 2021). These co-contaminants reduce the efficiency of ion exchange (IX) process and adsorption on granular activated carbon technologies for the removal of PFAS in leachate as they compete with PFAS contaminants for the adsorbent sites (Singh et al., 2021). It is to be noted that due to non-selective reactions between reactive species and co-contaminants in the bulk solution the advanced oxidation process is also considered ineffective (Mahinroosta & Senevirathna, 2020; Singh et al., 2021). Some recent technologies like electrochemical methods (Maldonado et al., 2021; Pierpaoli et al., 2021; Witt, 2021) and plasma reactors (Singh et al., 2021) have been proposed for PFAS treatment in the leachate as well. But both electrochemical and plasma technique are considered costly. **Figure 1** summarizes the technologies that have been used for the removal of PFAS.

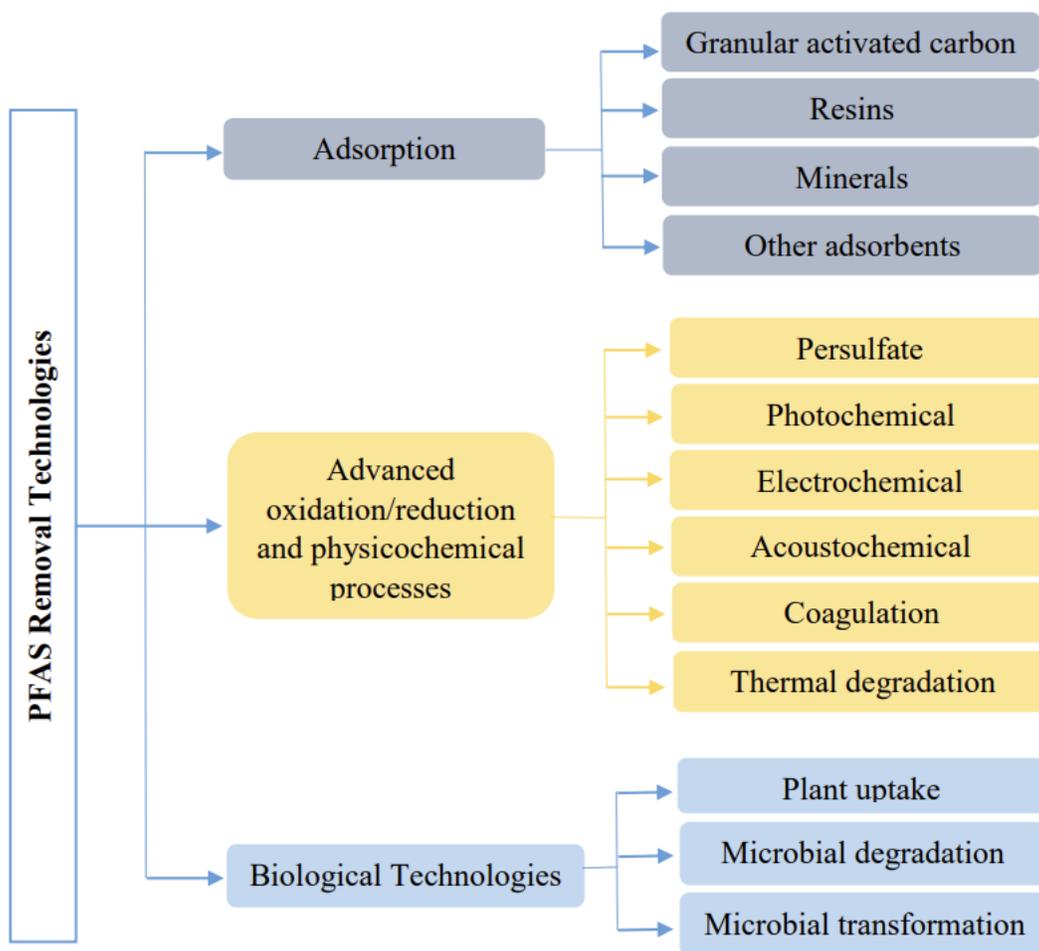


Figure 1: Technologies for removal of PFAS (Qi et al., 2022).

Photocatalytic degradation has gained more attention due to its straightforward operation and effective degradation under mild conditions (Xu et al., 2020; Zhu et al., 2021). As shown in **Figure 2**, photocatalysis is a light-initiated process where a photocatalyst after absorbing a suitable wavelength of light generates charge carriers in the form of electrons and holes (e^-/h^+) pairs, these electrons and holes are responsible for the execution of numerous oxidation and reduction reactions (Wei et al., 2019). Excited (e^-) produce radical such as superoxide (O_2^-) while the energetic holes (h^+) react with H_2O to produce hydroxyl (OH) radicals (Wei et al., 2019).

Titanium dioxide (TiO₂) and titanium-based photocatalytic materials are considered as suitable photocatalysts for the advanced oxidation processes because of their low cost, chemical stability, and efficiency (Zhu et al., 2021). But when plain TiO₂ is used for PFOS degradation, it has been associated with some drawbacks, like 1) its large bandgap energy (3.3 eV) limiting its photosynthesis activity in UV range only, 2) low efficiency in separation of excited electron-hole (e⁻/h⁺) pairs, 3) low adsorption and 4) low degradation efficiency (Li et al., 2020; Zhu et al., 2021). To solve this issue, TiO₂ was modified and doped with transitional and noble metals, which facilitates the transfer of photogenerated electrons, inhibits recombination of electron-hole, and increases the photocatalytic activity of the material (Li et al., 2020; Zhu et al., 2021). Moreover, to increase the specific surface area of TiO₂, several mixed composites have been reported with carbon based materials like activated carbon. The TNTs@AC is synchronized mixture of an adsorbent and photocatalysts to execute both processes simultaneously.

Previously our group developed titanate nanotubes (TNTs@AC) composite using AC and TiO₂ via hydrothermal synthesis route (Liu et al., 2016; Zhu et al., 2022). The TNTs@AC was capable of pre-concentrating low concentrations of pollutants onto the photoactive surface and finally degrading the chemical (Zhu et al., 2022). To improve the performance of TNTs@AC, it was doped with Fe²⁺ (Fe/TNTs@AC) for the removal of PFOA in water (Li et al., 2020) and removal of PFAS in landfill leachate (Tian et al., 2021). Another variants like Ga/TNTs@AC and Bi/TNTs@AC have been also developed and applied for the removal and degradation of GenX and PFOS in water respectively. (Zhu et al., 2022; Zhu et al., 2021). Degradation of PFOA initiated with the partition and cleavage of C – C bond at the head via produced holes or electrons (Bahnemann et al., 1997; Estrellan et al., 2010; Li et al., 2020). In this process the PFOA head group COO⁻ is decarboxylated via hole-mediate oxidation or electron transfer, which activate

molecules and commence a de-fluorination by losing CF_2 at each step as shown in Eq. (1) to (3) (Li et al., 2020; Zhong et al., 2019). In this process $(\text{C}_n\text{F}_{2n+1}\bullet)$ react with reactive oxygen species or OH to make the chain shorter (Li et al., 2020).

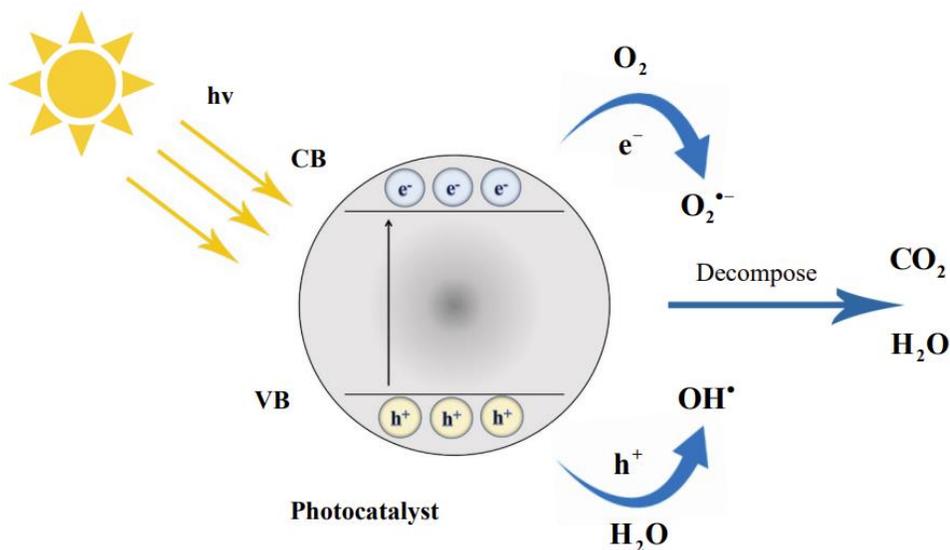


Figure 2: Photocatalytic working mechanism



The effectiveness of Bi-based photocatalytic material has been reported for the degradation of PFAS and persistent organic pollutants (POPs) (Dong et al., 2015; Weng et al., 2013; Zhu et al., 2022). Zhu et al, (2022) reported the Bi/TNTs@AC composite for the adsorption and subsequent solid-phase photo-degradation of GenX. In this research the Bi/TNTs@AC was able to adsorb 100 $\mu\text{g/L}$ of GenX within 1 h, degrade 70.0% and mineralize 42.7% of pre-sorbed GenX under UV (254 nm) in 4 hours.

1.2: Objectives

Degradation of PFAS in landfill leachate is considered very challenging compared to in water due to its complex matrices (Tian et al., 2021). Typically, landfill leachate contains high concentrations of dissolved organic matter (DOM), chloride, sulfate, ammonium, and metal ions, which interfere with the adsorption and photodegradation of PFAS (Tian et al., 2021). Because limited research has been reported for PFAS degradation in landfill leachate, the overall goal of this study was to test a two-step “Concentrate-&-Destroy” technique using an adsorptive photocatalyst, Bi/TNTs@AC, for more effective removal and degradation of PFAS in landfill leachate. The specific objectives of this study were to:

1. Prepare of the desired Bi/TNTs@AC composite based on commercially available activated carbon (AC) and TiO₂ under alkaline hydrothermal condition.
2. Measure the adsorption capacity and kinetics of PFOA
3. Test the subsequent solid-phase photodegradation of PFOA under UV irradiation (wavelength = 254 nm, intensity = 210w/m²)
4. Explore ways to enhance the photodegradation effectiveness (pH, temperature, oxidants, and of Fe³⁺)
5. Examine the reusability of the materials without invoking chemical regeneration.

1.3: Collection and characterization of landfill leachate samples

Leachate samples were collected from Coffee County Landfill, located at 7733 AL-125, Elba, AL 36323, USA. This landfill serves Coffee County, Enterprise County, the City of Elba, Fort Rucker, and City of New Brockton, and gets all the municipal solid waste (MSW) from Pike, Dale, Geneva, Henry, and Covington. It should be noted that it is permitted to serve Alabama, Georgia, Florida, and Mississippi with the site's with an incoming waste of around 80% MSW, 18% plastic shreds and sludge, and 2% construction, demolition, and other commercial and industrial waste. At the time when leachate was collected by our colleague, Cell 7 was their active disposal area and covered 14 acres, and along with their other cells have their leachate feed into a single above-ground storage tank. The leachate from all the landfill cells mixes together and allows for some gravity settling before being emptied by the tanks, which occurs roughly 1-2 times a quarter. When our samples has collected the tank was emptied two months ago and the leachate was thoroughly mixed and fresh and no further mixing was needed in the lab. We collected a total of 50 gallons of raw landfill leachate in ten 5-gallon HDPE buckets and lids. During sampling, the temperature of the area was 68°F, with a cloud overcast for the early morning and late evening, while the sky was clear when our colleague arrived at 2:00 pm, with 10% humidity.

Once the samples were carried out in the lab the leachate was filtered first with a course membrane filter, then a fine membrane filter, and then a 5µm mixed cellulose ester (MCE) membrane filter. All the filtered leachate is stored in a laboratory inside the refrigerator at ~4°C in 5 gallons of HDPE buckets. When leachate is needed for experiment, we carefully fill a 1 L glass bottles or long-neck flask form the top of the buckets that none of the settled particles should be

re-suspended. When we fill the bottle with leachate, we are going to spiked it with target PFAS to analyze that specific PFAS interaction with our absorptive and photocatalyst synthesized material.

1.4: Leachate characterization

Table 1 summarizes the concentration of PFAS and other element concentrations in the leachate sample it was filtered. 18 PFAS were detected in the landfill leachate. Among the detected PFAS the highest concentration were PFBS (8058-8251 ng/L), PFHxA (4663-4847 ng/L), PFBA (3060-3370 ng/L), PFPeA (1424-1520 ng/L), 6:2 FTS (882-1520 ng/L), PFOA (959-1068 ng/L), PFHxS (611-769 ng/L), PFHpA (405-435 ng/L) and PFOS (191-239 ng/L). It looks that short-chain PFAS are dominant in the landfill leachate, which is related to the conversion of long-chain PFAS and its precursor to short-chain through the complex biogeochemical process inside landfill leachate and chemical and photochemical process in the natural environment (Li et al., 2020; Tian et al., 2021; Wei et al., 2019). Also, it can be seen that landfill leachate also contains a high concentration of total dissolved solids (TDS), Magnesium, Potassium, and Sodium. Elements which their concentration was <0.1 mg/L is not shown in the table 1.

Table 1: PFAS and other elements in leachate sample

Final concentration (mean \pm standard deviation, ng/L)		
PFAS		Filtered Leachate
	PFBA	2884 \pm 91
	PFPeA	1288 \pm 26
	PFBS	8186 \pm 496
	4:2 FTS	11 \pm 3
	PFHxA	4546 \pm 186
	PFPeS	92 \pm 18
	HFPO-DA	< 250
	PFHpA	381 \pm 13
	PFHxS	687 \pm 56
	PFHpS	17 \pm 1
	PFOA	947 \pm 7
	6:2 FTS	1035 \pm 108
	PFOS	254 \pm 5
	PFNA	75 \pm 10
	PFDA	55 \pm 7
	8:2 FTS	24 \pm 7
	N-MeFOSAA	88 \pm 3
N-EtFOSAA	58 \pm 4	
Average concentration (mg/L)		
Other elements	Boron	7.2
	Calcium	50.0
	Iron	3.4
	Magnesium	105.7
	Potassium	389.0
	Sodium	2167.3
	Nitrate-N	4.3
	Hardness (CaCO ₃)	558.3
	Alkalinity (CaCO ₃ equiv.)	5574.3
	Sulfate-Sulfur	115.3
	TDS	9408.0

Chapter 2. Materials and Methods

2.1: Chemicals

All the chemical that was used for the experiment were analytical grade or higher (Tian et al., 2021). Nano-TiO₂ (P-25, 80% anatase and 20% rutile) was purchased from Evonik Industries (Worms, Germany). Filtrosorb-400® granular activated carbon (GAC) (F400) was purchased from Calgon Carbon Corporation (PA, USA). PFOA was acquired from Sigma-Aldrich (St. Louis, MO, USA). Perfluoro-n-[1,2,3,4,5,6,7,8-¹³C₈]octanoic acid (¹³C-PFOA or M8PFOA) was purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada), and was used as an isotopically-labeled internal standard. All solutions were prepared using deionized (DI) water (18.2 MΩ cm, Millipore Co., USA). Sodium hydroxide (pellets), Bismuth nitrate pentahydrate, iron (III) chloride hexaydrate, potassium per sulfate and other chemicals were obtained from VWR International (Radnor, PA, USA).

2.2: Preparation of Bi/TNTs@AC

Bi/TNTs@AC was synthesized through hydrothermal process (Liu et al., 2016; Zhu et al., 2022). In the first step, the TNTs@AC was prepared by adding 1.2 g of AC with 1.2 g of TiO₂ and they were thoroughly mixed with 66.7 mL of 10 M NaOH solution. After magnetic stirring of the mixture for 12 h, it was transferred in to a 100 mL Teflon reactor covered with stainless-steel and heated at 130 °C for 72 h (Zhu et al., 2021).The grey precipitate (TNTs@AC) was washed with DI water until the pH got neutral (pH=7.0±0.5), and then the material was oven dried at 105°C for 24 h (Zhu et al., 2021).

In the next step, 1 g of oven-dried prepared TNTs@AC was dispersed into 80 mL of DI water, then 6 mL of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution (5 g/L as Bi, pH = 0.83) was added dropwise into TNTs@AC solution under continues stirring over the pH range of 4-6. The pH was adjusted by using on 1 M of NaOH solution. After the 3 h of mixing, the precipitate was removed after 24 h of gravity settling and then oven dried for 24 h. Based on the Bi percentage mass content, the synthesized material was as tagged as 3%Bi/TNTs@AC. Eventually, the material was calcined at 550°C for 5.5 h under nitrogen flow of 100 mL/min (Tian et al., 2021). **Figure 3**, shows the procedure of preparing the Bi/TNTs@AC.

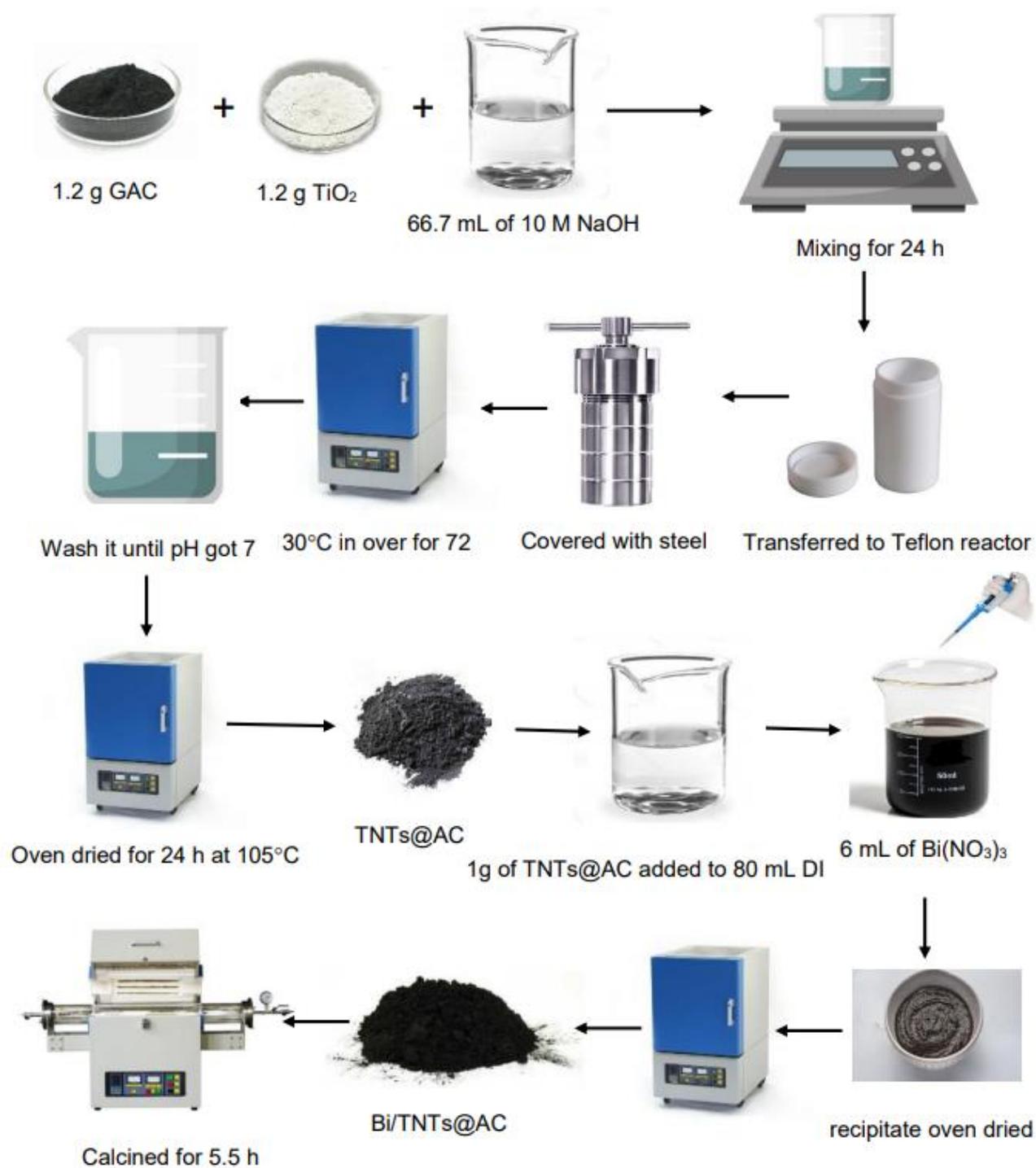


Figure 3: Synthesis of Bi/TNTs@AC composite.

2.3: Adsorption and Photo-degradation of PFAS in Leachate by Bi/TNTs@AC

2.3.1: Adsorption kinetic tests

The batch adsorption kinetics test were conducted using 50 mL high density polypropylene (HDPE) vials. The adsorption of PFOA was initiated by adding 0.2 g (5 g/L) of 3%Bi/TNTs@AC in 40 mL of a leachate sample spiked with 100 µg/L of PFOA at pH=9.4±0.2. The vials were fully covered with aluminum foil to avoid any light exposure and were placed on rotator at 70 rpm located in an incubator at 25°C. samples were taken at predetermined time intervals (0.5, 1, 4, 8, 16, and 24 h). The solids were separated by centrifugation (4000 rpm, 3 min) and the supernatant was analyzed for remaining PFOA in the aqueous phase. To assure data quality, all tests were carried out in duplicate (Tian et al., 2021).

2.3.2: Solid phase extraction (SPE) and analysis of remaining PFOA.

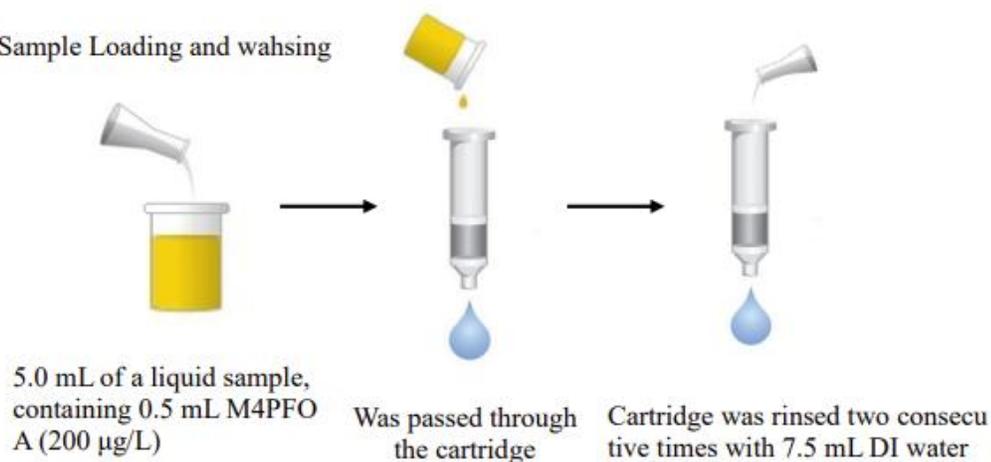
In order to prevent the potential landfill leachate matrix interferences and its effect with the PFOA analysis, solid phase extraction (SPE) was carried out to extract PFOA from the liquid samples (Tian et al., 2021). First of all, one day before the experiment was carried out, two 50 mL (HDPE) vials was pre-cleaned with 5 mL methanol and 5 mL acetone. Secondly, an ISOLUTE ENV+ SPE cartridge (200 mg/6 mL) was taken and placed under vacuum for conditioning. At this stage first of all, 10 mL of methanol at the rate of 1 drop/s was passed through the cartridge, after fully passing of the methanol, 10 mL of 1 % acetic acid was passed through the cartridge and followed 10 mL of DI water. Third, 5.0 mL of a liquid sample, which contained 0.5 mL M4PFOA (200 µg/L), was passed through the cartridge. Fourth, the cartridge was washed with 7.5 mL DI

water twice. Fifth, the target PFOA was collected with 5 mL methanol at a rate of 1 drop/s in the pre-cleaned polypropylene vial which prepared a day before. This step was repeated with another pre-cleaned vials. The collected eluents were then combined into a single vials and concentrated to 2 mL under a flow of high-purity nitrogen. Finally, 1 mL of the concentrated sample was taken and combined with 0.8 mL DI water and 0.2 mL internal standard (M8PFOA, 200 µg/L) for further analysis. The samples were stored at 4 °C for LCMS analysis (Tian et al., 2021). The **Figure 4** could easily illustrate the SPE procedure.

Step 1: Conditioning



Step 2: Sample Loading and washing



Step 3: Collecting and concentrating

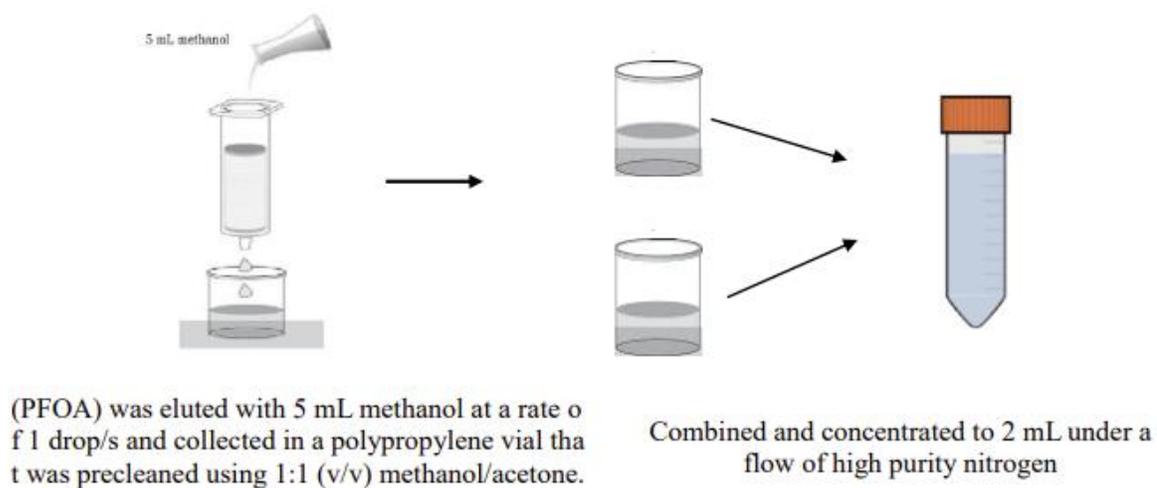


Figure 4: Procedure of solid phase extraction.

2.3.3: Photo-degradation of PFOA

The batch photo degradation test was carried out following the adsorption kinetic test. The solids were separated by centrifugation (4000 rpm, 3 min) after the removal of around 99% of the supernatant and the remaining solid/water mixture was transferred into a quartz dish (OD×H = 6×1.6 cm) equipped with a quartz cover. Subsequently, 10 mL of DI water was added to the mixture, and the pH was kept to 9.4±0.2 as it was the landfill leachate initial pH. Then, it was placed in a Rayonet UV-reactor reactor (Southern New England Ultraviolet CO., Branford, CT, USA) operated at a wavelength of 254 nm and an intensity of 210 W/m². The temperature of the photo reactor was kept between 36 –40°C when the test was performed. The photocatalytic degradation test lasted for 4 hours, during which the sample was thoroughly mixed and stirred manually every 30 minutes to facilitate the UV exposure to the material (Zhu et al., 2021). After the photoreaction, 5 mL of the supernatant was carefully filtered through a 0.22 µm PES membrane, and the filtrate was analyzed for fluoride using a Dionnex Ion chromatography. The defluorination of PFOA was estimated based on the fluoride concentration in the solid phase that was adsorbed on the material (Bi/TNTs@AC) surface during adsorption test and then degrade in the form of fluoride during the photodegradation stage (Zhu et al., 2021). All tests were carried out in duplicate.

2.4: Effect of experimental conditions on solid-phase photodegradation of PFOA

Photodegradation test were performed to evaluate the effect of pH, potassium per-sulfate, ferric chloride and temperature effect on solid phase photodegradation of PFOA on Bi/TNTs@AC.

It is to be noted that, PFOA and other PFAS was spiked in landfill leachate then adsorbed through adsorption kinetic test to Bi/TNTs@AC. The experimental condition was follow: Bi/TNTs@AC = 0.2 g, spiked leachate sample with 100 $\mu\text{g/L}$ PFOA = 40 mL, pH = 9.4, equilibrium time 24 h. The PFAS laden were removed and then exposed to UV light for 4 h under the same condition as explained before under different pH level and different concentration of FeCl_3 and $\text{K}_2\text{S}_2\text{O}_8$.

2.5: Chemical Analysis

PFAS in quantity was analyzed via ultra-performance liquid chromatography-tandem mass spectrometer (UPLC-MS/MS). The aqueous fluoride (F^-) concentration was analyzed via ion chromatography (IC) (Dionex, CA, USA) with an anion exchange column (Dionex Ionpac AS22) and anion dynamically regenerated suppressor (ADRS 600, 4mm) (Zhu et al., 2021). The Bi and Ti solution were analyzed and measured via inductively coupled plasma-optical emission spectroscopy (ICP-OES, 710-ES, Varian, USA), with detection limit of 100 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$, for Bi and Ti respectively (Zhu et al., 2022).

Chapter 3. Results and discussion

3.1: Adsorption kinetic tests

Figure 5 presents the adsorption kinetic data of spiked leachate with 100 $\mu\text{g/L}$ PFOA as a model PFAS by 3% Bi/TNTs/AC. The adsorption kinetic test were performed at the time interval of 0.5, 1, 4, 8, 16, and 24 h. The PFOA removal approached to >95% after 24 h. The higher removal efficiency of 3%Bi/TNTs/AC can be credited to the high surface area and pore structure. The adsorption is primarily governed by the hydrophobic interactions (Liu et al., 2018) because the adsorption tests were performed at the original pH of leachate (pH = 9.4). Moreover, the efficient removal of PFOA from a complex matrix system of leachate shows that the sites of Bi/TNTs/AC are accessible for PFOA adsorption.

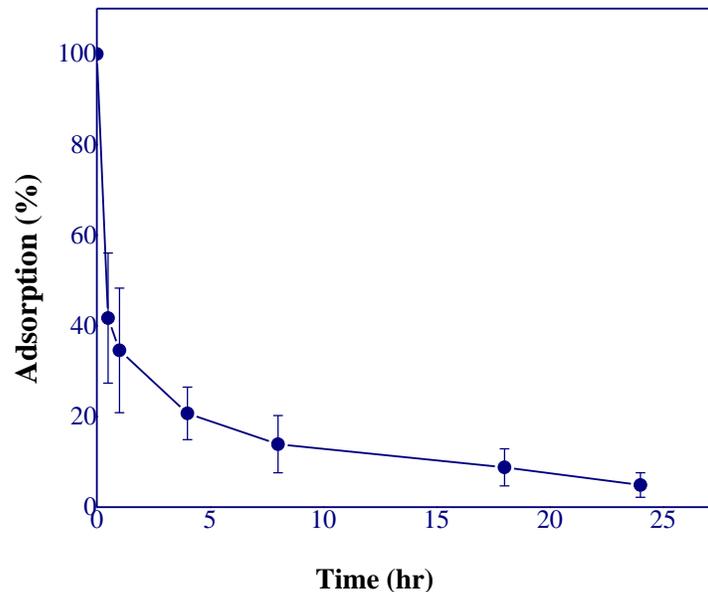


Figure 5: Adsorption kinetics of PFOA from a model landfill leachate by 3%Bi/TNTs/AC
Experimental conditions: spiked PFOA concentration = 100.947 $\mu\text{g/L}$, material dosage 5g/L, pH = 9.4 \pm 0.2.

3.2: Effect of pH on photocatalytic defluorination of PFOA

To consider the effect of pH and enhance the PFOA degradation, the solid-phase photodegradation of spiked leachate was carried at different pH level. It is mentionable that the pH was 9.4 ± 2 during the adsorption phase and was done at the same manner that we adopted before. During the photocatalytic degradation, tests were carried out at pH levels, i.e. 5.0, 7.0, 9.4, 10.5 and 11.5 ± 2 . It is to be noted that the pH was adjusted by using 1 M NaOH and 1 M HCl solution during the solid-phase photodegradation phase. After the photocatalytic reaction, 5 mL of the supernatant was carefully filtered through a $0.22 \mu\text{m}$ PES membrane, and the filtrate was analyzed for F^- using an ion chromatograph (Dionex, USA) equipped with an Ionpac AS22 column and an anion dynamically regenerated suppressor (ADRS, 600), with sodium carbonate and bicarbonate as the eluent (flow rate 1.2 mL min^{-1}). The detection limit for F^- was $10 \mu\text{g L}^{-1}$.

Figure 6 shows that at original leachate pH (9.4 ± 0.2), the 3%Bi/TNTs/AC composite showed around 46% defluorination activity, which decreased to 19.25 % and 6.02 % at pH 7.0 and 5.0, respectively. While, with the increase of pH from 9.4 to 10.5 and 11.5 ± 2 the defluorination activity also increase to 61% and 75% accordingly. Based on the Hpzc (6.3 for Bi/TNTs, **Figure 7**), a negative surface charge is expected for 3%Bi/TNTs@AC above pH 6.3 (Zhu et al., 2022), which means that electrostatic interactions between PFOA and 3%Bi/TNTs@AC is more favorable at alkaline pH range. While in neutral and acidic pH range the surface potential of 3%Bi/TNTs turned more positive and as a result the interaction in is considered to much more unfavorable with the functional group of PFOA (carboxylate) (Zhu et al., 2022).

The mechanism seems to be reductive degradation pathway and the alkaline condition are favorable for the generation of hydrated electron (e^-_{aq}). The hydrated electrons (e^-_{aq}) are considered

one of the strongest reductive species ($E = -2.9$ V) for breaking down the PFAS, C–F bond (Ren et al., 2021) . The production of hydrated electron is restricted in acidic condition due to the presence of free proton via Eq. (4) and (5) which easily annihilate them hence no charge separation takes place (Gu et al., 2017).

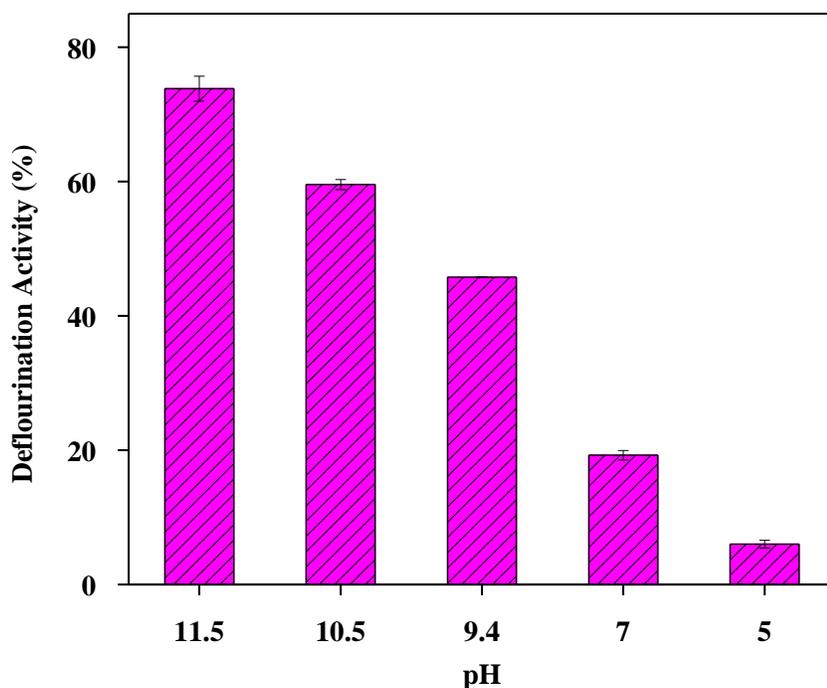


Figure 6: Effect of pH on photocatalytic defluorination of PFOA pre-adsorbed on 3%Bi/TNTs@AC. Adsorption test conditions: initial PFOA in leachate = 100.947 $\mu\text{g/L}$, 3%Bi/TNTs@AC = 5 g/L, time 24 hours, temperature = $22 \pm 1^\circ\text{C}$; Photodegradation conditions: UV intensity = 210 W/m^2 and irradiation time = 4 h.

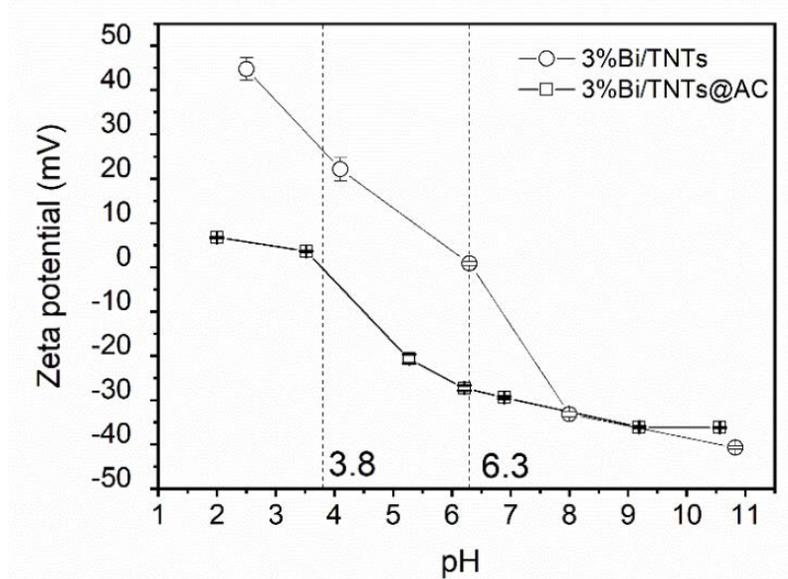
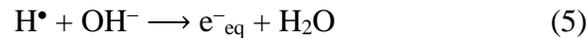
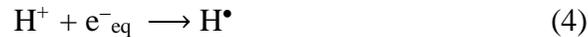


Figure 7: Zeta potential of 3%Bi/TNTs@AC and 3%Bi/TNTs as a function of pH (Zhu et al., 2022).



3.3: Effect of persulfate ($\text{K}_2\text{S}_2\text{O}_8$) on the solid-phase photocatalytic degradation of PFOA

Persulfate ($\text{S}_2\text{O}_8^{2-}$) was used to further enhance the rate of PFOA photocatalytic degradation. Persulfate has been widely accepted for enhancing photocatalytic degradation due to the high oxidative potential ($E^0 = 2.1 \text{ eV}$) of $\text{SO}_4^{\bullet-}$ species, which can be activated to achieve even higher oxidative potential (2.6 eV) by generating free sulfate radicals ($\text{SO}_4^{\bullet-}$) (Tsitonaki et al., 2010; Yang et al., 2019). When persulfate is heated (Hori et al., 2010; L. Yang et al., 2020) or exposed to light (Lau et al., 2007) it generate free $\text{SO}_4^{\bullet-}$ radical which is used for degradation of

PFOA (Waclawek et al., 2017; S. Yang et al., 2020). As shown in Eq. (6), we tested the effects of persulfate at three different concentrations of persulfate. As shown in **Figure 8**, the presence of 100 μM of $\text{S}_2\text{O}_8^{2-}$ resulted in the optimal defluorination activity (55.41 %). The tests were carried out at pH 9.4 indicating the activation of persulfate under alkaline conditions.

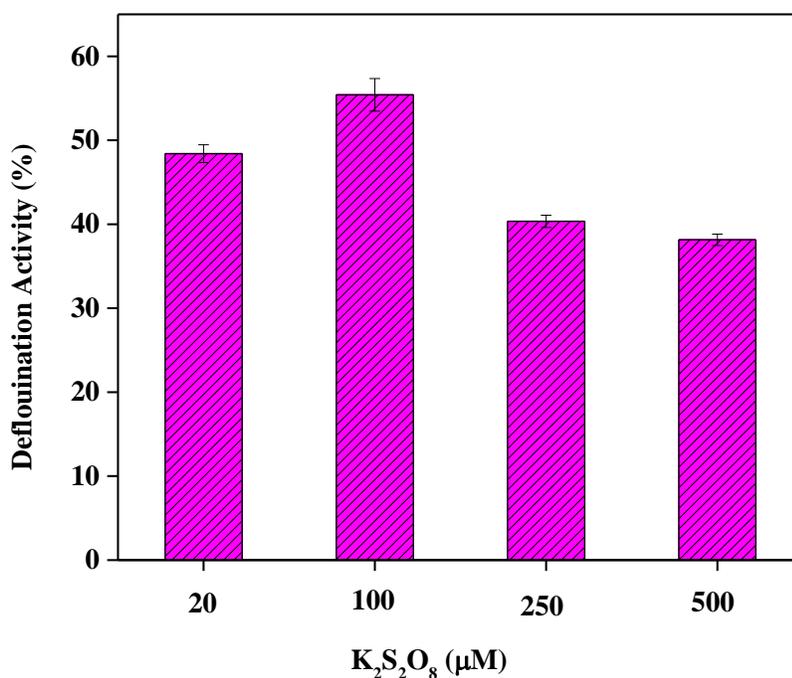
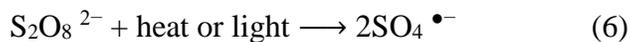
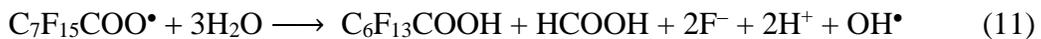
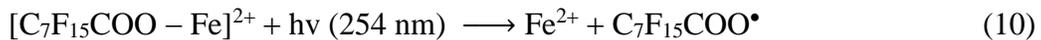


Figure 8: Effect of persulfate concentration on photocatalytic degradation of PFOA
 Adsorption conditions: Initial PFOA = 100.947 $\mu\text{g/L}$, 3%Bi/TNTs@AC = 5 g/L, Time 24 hours, Temperature = 22 ± 1 , and pH = 9.4 ± 0.2 ; Photodegradation conditions: UV intensity = 210 W/m^2 , irradiation time = 4 h, and pH = 9.4 ± 0.2 .

3.4: Effect of Fe³⁺ on photocatalytic degradation of PFOA

To test the effect of Fe³⁺, the photocatalytic degradation tests were carried out in the presence of three different concentration levels of Fe³⁺ under 4 h UV irradiation. **Figure 9** shows that the presence of Fe³⁺ remarkably increased the defluorination rate, with the highest defluorination (57.72 %) observed at a Fe³⁺ dosage of 60 μM at pH = 9.4. The effect may be attributed to the following reasons. First, DOM are able to form complexes with different absorbent in the presence of Fe³⁺, and as a result promote the degradation of organic pollutant (Qi et al., 2022; Zhu et al., 2022). Specifically in the presence of light, Fe³⁺ and DOM by initiating a ligand-to-metal electron transfer, produces Fe²⁺ and a DOM radical (DOM^{•+}) Eq. (7) (Gaberell et al., 2003). Then DOM^{•+} radical in the presence of oxygen generate O₂^{•-} radical Eq. (8) (Gaberell et al., 2003) which could be used for degradation of PFOA. Second, the effect may be attributed to the complexation of Fe³⁺ with the PFOA, then this complex is excited by the presence of 254 nm UV light as Eq. (8) and (9) (Wang et al., 2008). Then the generated radical in the presence of water produce formic acid, fluoride ion and C₆F₁₃COOH with less CF₂ than original PFOA as shown in Eq. (11) (Wang et al., 2008).



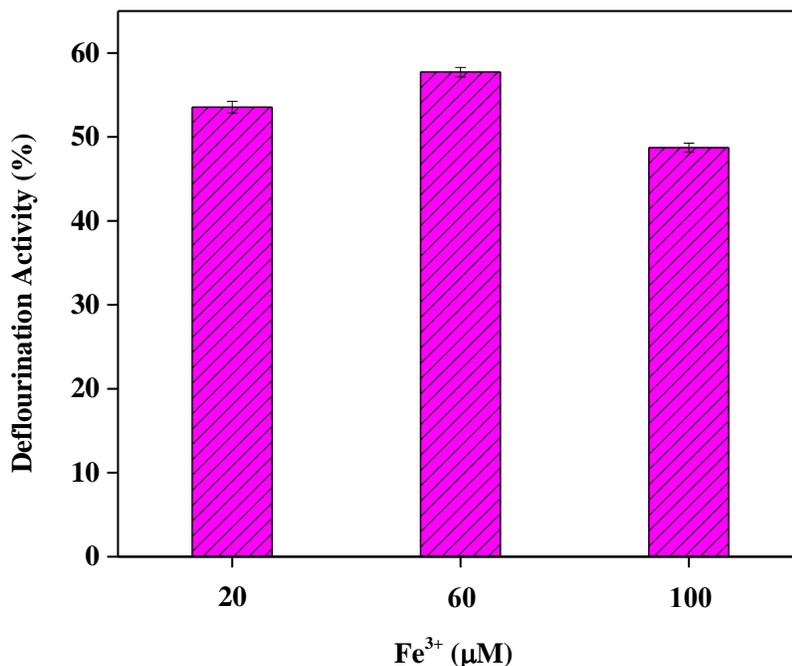


Figure 9: Effect of Fe³⁺ on photocatalytic degradation of PFOA. Adsorption conditions: initial PFOA = 100.947 μg/L, 3%Bi/TNTs@AC = 5g/L, Time 24 hours, Temperature =22 ±1, and pH = 9.4±0.2; Photodegradation conditions: UV intensity = 210 W/m², irradiation time = 4 h, and pH = 9.4±0.2.

3.5: Effect of temperature on photocatalytic degradation of PFOA

Figure 10 shows the effect of temperature on photocatalytic degradation of PFOA, during photo degradation. The defluorination activity increase from 46% to around 54% when the temperature was increased from 38°C to 63°C. The reason for this increase could be associated with the promoted the quantum efficiency and higher reactant kinetics resulting in the increase of photodegradation of PFOA (Zhang et al., 2016). It is to be noted that the quantum efficiency

indicates the increase in proportion of PFOA molecule that exist in excited state where they are involved and initiate the degradation process (Zhang et al., 2016).

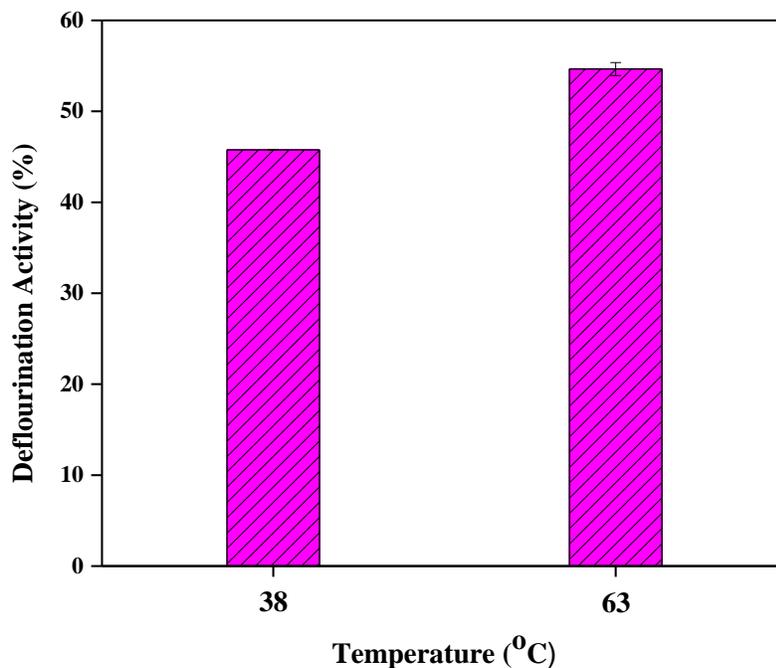


Figure 10: Effect of temperature on photodegradation of PFOA. Adsorption conditions: initial PFOA = 100.947 $\mu\text{g/L}$, 3%Bi/TNTs@AC = 5g/L, time = 24 hours, pH = 9.4 \pm 0.2; Photodegradation conditions: UV intensity = 210 W/m², irradiation time = 4 h, and pH = 9.4 \pm 0.2.

3.6: Conclusions

An adsorptive photocatalyst, Bi/TNTs@AC, was prepared and tested for the removal and subsequent photodegradation of PFOA in a model landfill leachate. Despite the strong matrix effect of the leachate, We have applied this material for PFOA adsorption and subsequent photodegradation, which was promising. We found that this material (3%Bi/TNTs@AC) was able to selectively adsorb >95% of PFOA in 24 h and able to defluorinate 46% of pre-adsorbed PFOA. Alkaline pH was more favorable for the photodegradation of PFOA possibly due to higher desorption of PFOA. Moreover, we found that the presence of Fe^{3+} , per-sulfate, and elevated temperature remarkably enhanced the solid-phase mineralization rate of PFOA. The findings indicated that 3%Bi/TNTs@AC appears to be a promising adsorptive photocatalytic material for a two-step adsorption and subsequent photo-degradation of PFOA in landfill leachate. Compared with conventional adsorption using AC or ion exchange resins, it not only eliminates the need for chemical regeneration, but also offers the capability to completely degrade or defluorinate PFAS; Compared to commonly used photocatalytic processes that treat a large volume of bulk water, it only treats a small volume of solids containing concentrated PFAS, and thus, requires much less energy input.

In the future work, it would be interesting to explore new strategies to enhance the adsorption selectivity to further facilitate the subsequent photo-degradation of PFAS using 3%Bi/TNTa@AC in landfill leachate. For example, we may further tailor the material to synergize various adsorption mechanisms. In addition, the combined effect of persulfate and temperature and/or cations during the photo-degradation phase should be explored. Moreover, the effects of various constituents of dissolved organic matter should be identified to further understand and mitigate the inhibitive effect.

Moreover, the adsorption and degradation of the multiple PFAS in the original leachate should be tested. To this end, two consecutive adsorption-photodegradation/regeneration tests will be performed using the original leachate sample and following the optimized adsorption and photodegradation protocols.

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