Fe-nanoparticles dispersed carbon micro and nanofibers: Surfactant-mediated preparation and application to the removal of gaseous VOCs

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\textbf{A B S T R A C T}

This study describes the preparation of Fe nanoparticle-dispersed carbon microfibers (Fe-ACFs) and carbon nanofibers (Fe-CNFs) for the removal of gaseous volatile organic compounds (VOCs). Fe-ACFs were prepared by impregnating ACFs with Fe salts. Three different types of surfactants (cationic, anionic, or non-ionic) were used to achieve the segregation and monodispersion of Fe(III) ions in aqueous solutions. Fe(III) nanoparticles were produced on the ACF-surface after the calcination of Fe(III)-surfactant molecules which were transferred from the solution to the ACF during the impregnation-step. Fe-CNFs were prepared by the catalytic chemical vapor deposition (CVD) of benzene on the Fe-ACFs used as a substrate. Different analytical instruments were used to characterize the physicochemical properties of the prepared materials, including the loading and monodispersity of the Fe nanoparticles. The data showed that Fe nanoparticles of 8-nm average size were uniformly dispersed over the surface of the ACFs with a maximum loading of 0.68 mg/g when using SDS, an anionic surfactant. In this case, the relatively more uniform and dense growth of CNFs was observed. The prepared Fe-ACFs and Fe-CNFs were used to remove carbon tetrachloride (CCl\textsubscript{4}), a persistent gaseous VOC. The results of the study show an effective method for preparing surfactant-enhanced Fe nanoparticles and carbon webs of micro- and nanofibers for the removal of persistent gaseous organic pollutants.

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1. Introduction

Currently, metal nanoparticles are used in a wide range of applications, for example, in drug delivery, optoelectronics, magnetics, biomedicine, and chemical reactions\textsuperscript{[1–5]}. The nanoparticles made of transition metals, such as nickel (Ni), iron (Fe), and cobalt (Co), are commonly used as catalysts for growing different carbon nanostructures, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), and carbon nanowires (CNWs)\textsuperscript{[6–9]}. In this context, there is an increasing focus on controlling the size and uniform dispersion of metal nanoparticles, especially on the surface of a porous substrate during the preparation of nanostructures. One way to achieve a controlled size and uniform dispersion of metal nanoparticles is the use of surfactants in the precursor solutions.

The literature is replete with the synthesis of metal oxide nanoparticles, such as FeO, CoO, AuO, AgO, and NiO, in either organic or aqueous solutions and using various commercially available surfactants, such as sodium dodecyl sulfate (SDS), tri-n-octylphosphine (TOPO), triton X-100, cetyl trimethylammonium bromide (CTAB), cetyl trimethylammonium chloride (CTAC), and cetylpyridinium chloride (CPC)\textsuperscript{[10–26]}. In these studies, metal nanoparticles were synthesized in the solutions by reducing the different metal-salts to their respective oxides using a strong reducing agent and aging at elevated temperature. Surfactants prevented the agglomeration of metal particles in the solution.

It is important to note that it is extremely difficult to prepare nanoparticles in their metallic state because the highly reactive nanoparticles are instantly converted into their respective oxide counterparts. Therefore, in this study, activated carbon fibers (ACFs) were first impregnated with ferric nitrate salts in the aqueous solution using a suitable surfactant. The surfactant prevented Fe(III) ions from agglomerating with neighboring ions in the impregnating solution. Fe(III) oxide nanoparticles were produced on the ACF-surface after the calcination of Fe(III)-surfactant molecules which were transferred from the solution to the ACF during the impregnation-step. Next, the metal oxides were converted into the
metallic state by a reduction under a hydrogen atmosphere. The Fe-ACFs thus prepared had a significant and uniform loading of Fe nanoparticles and were subsequently used as a substrate for growing CNFs by catalytic chemical vapor deposition (CVD). The prepared Fe-ACFs and Fe-CNFs were used in removing carbon tetrachloride (CCl₄), a persistent gaseous volatile organic compound (VOC).

CCl₄ is a major hazardous chemical because of its high toxicity and carcinogenicity [27]. It is stable at room temperature, and also, may bioaccumulate in tissues, which may cause adverse health effects. CCl₄ is also categorized as a chemical warfare agent (CWA) [28]. CCl₄ has been removed by different methods (including adsorption, oxidation, and catalytic hydrolysis) and using different materials (such as the oxides of iron (Fe) and silver (Ag), activated carbon (AC), and granular activated carbon (GAC)) [27,29–34]. CCl₄ has also been removed by adsorption onto ACFs modified with different metals, such as chromium (Cr), copper (Cu), and silver (Ag) [28]. In another study, CCl₄ has been removed by bentonite-modified ammonium salts [34]. Among these materials, Fe or FeO are relatively more effective in removing CCl₄ by catalytic destruction. Considering the significantly large BET surface areas of ACFs and CNFs, the present study was undertaken to modify the ACFs and CNFs with Fe and then to utilize the Fe-impregnated ACFs and CNFs for the catalytic/adsorptive removal of CCl₄. In the latter material (Fe-CNFs), the Fe had dual roles: (1) to grow CNFs on ACFs by CVD and (2) to remove the organic species. Herein, it may be noted that the surface-functionalized ACFs and CNFs have been shown to be successful adsorbents in different environmental remediation applications, ranging from the removal of arsenic, fluorides, and phenol in water to that of SO₂, NOₓ, and 2-chloroethanol in air [35–39].

2. Materials and methods

ACFs were impregnated with hydrated ferric nitrate using three different types of surfactants: (1) SDS, an anionic surfactant, (2) TOPO, a cationic surfactant, or (3) Triton X-100, a non-ionic surfactant. Fig. 1 presents the chemical structure of the surfactant molecules. SDS is an organosulfate compound consisting of a 12-carbon tail attached to the sulfate functional group, TOPO is an organophosphorus compound having uncharged alkyl chains. It also has polarity resulting from the dipolar phosphorus-oxygen (P=O) bond. TOPO is a commonly used cationic surfactant to prepare and stabilize the Fe-nanoparticles [40]. The triton molecule is neutral. In general, anionic and non-ionic surfactants facilitate the formation of small and large nanoparticles, respectively. In addition, the size and stability of the nanoparticles depend on the surface charge of the surfactant molecules and the interaction between the surfactant molecules and the metal ions [21,41,42].

In this study, the Fe-ACFs and Fe-CNFs prepared using SDS exhibited relatively superior physiochemical properties that are responsible for the enhanced adsorption capacity for CCl₄. During impregnation, the negatively charged hydrophilic head of SDS molecule binds to the positively charged Fe(III) ions produced in the solution following the dissolution of Fe salts, which prevents Fe(III) ions from agglomerating with neighboring ions. Consequently, an increasingly large amount of Fe(III) ions is transferred from the bulk solution to the ACF-surface, along with SDS. During the calcination step, SDS decomposes, which leaves behind Fe(III) oxide nanoparticles on the ACF-surface. Subsequent reduction in H₂-atmosphere converts Fe(III) particles into their pure metallic state, i.e., Fe(0) that have been further reduced in size. Fig. 2 schematically depicts the above effects.

In the case of cationic TOPO, it has the polarity resulting from the dipolar phosphorus–oxygen (P=O) bond. The electrostatic repulsion occurs between the surfactant molecule and the Fe(III) ions in the impregning solution which inhibits the attachment of the surfactant to the Fe(III) ions. Therefore, the segregation of the Fe(III) ions or monodispersity in the impregnating solution is reduced. Triton X-100 is a neutral molecule and does not attach to Fe(III) ions. As discussed later in the manuscript, the size of Fe(0) nanoparticles on the Fe-ACFs surface was found to be smaller for SDS than for the other two surfactants (TOPO and Triton). Consequently, the CNFs grown on the ACFs in the former case were relatively denser and more uniform. The CCl₄ adsorption capacity of the Fe-ACFs and Fe-CNFs was also relatively larger when the materials were prepared using SDS.

2.1. Materials

Fe(NO₃)₃·9H₂O (purity > 99.9%), SDS (purity > 90%), Triton X-100 (purity > 99%), and benzene (purity > 99.9%) were purchased from Merck, Germany. TOPO (purity > 98%) was purchased from Alfa Aesar, Germany. The phenolic resin precursor-based ACFs were purchased from Kynol Inc., Tokyo (Japan). Hydrogen (purity > 99.999%), zero air (purity > 99.999%), nitrogen (purity > 99.999%), and CCl₄ were purchased from Sigma Gases, India.

2.2. Synthesis of Fe-dispersed ACFs (Fe-ACFs)

The as-received ACFs samples were leached for 6 h in de-ionized (DI) water at 80 °C to leach out any undesirable ions from the ACFs surface to make it conducive to metal impregnation. After leaching, the wet samples were dried for 4 h in static air at room temperature (30 ± 5 °C), which was followed by oven-drying for 12 h at 120 °C. Approximately 1.5 g of the oven-dried ACFs sample was wrapped over a perforated glass tubular reactor and then vacuum-dried for 12 h at 200 °C to remove any entrapped gases from the pores of ACFs. After drying, the ACFs sample was slowly cooled to room temperature (30 ± 5 °C).

Fe(NO₃)₃·9H₂O salts were used as an iron precursor for preparing the Fe-ACFs. The impregnating solution of Fe(NO₃)₃·9H₂O was prepared in DI water at various molar concentrations (0.1–1 M) by the incipient wetness impregnation method [36]. The Fe
concentration was optimal at 0.4 M for preparing the Fe-ACFs. Different surfactant concentrations (0.1, 0.3, or 0.5%, w/w) were used for impregnation. The surfactant at a specific concentration was added to 150 mL of the solution and mixed vigorously for 30 min. Next, the impregnating solution was recycled using a peristaltic pump through the perforated tubular reactor wrapped with the ACFs. The impregnation time was 6 h.

After impregnation, the wet samples were dried in static air for 4 h at room temperature, which was followed by oven-drying for 12 h at 120 °C before calcination and reduction under an H2 atmosphere. Calcination and reduction were carried out in indirect heat in the programmable, electric, and horizontal furnace shown in Fig. 3. Calcination and reduction were carried out at 400 °C for 4 h and 500 °C for 2 h, respectively. The flowrate of N2 during calcination and that of hydrogen during reduction was 0.15 standard liters per min (slpm). Some samples of Fe-ACF were also prepared without using surfactant. For the reference purpose, such samples are denoted in the manuscript as Fe-ACF(ws).

2.3. CNF synthesis and growth mechanism

CNFs were grown on Fe-ACFs in the same horizontal furnace that was used for calcination and reduction. N2 gas was bubbled through liquid benzene (C6H6) at a flowrate of 0.2 slpm. The bubbling temperature was adjusted to a predetermined saturation temperature corresponding to the desired concentration (~14,000 ppm or 1.4%, v/v) of benzene vapor in the N2. The gaseous mixture was delivered to the horizontal CVD reactor containing a SS-mesh on which the Fe-ACFs sample was placed. The CVD was carried out at 800 °C and 1 atm by decomposing the hydrocarbon feed stock (i.e., C6H6 + N2). The Fe dispersed in ACFs catalyzed the growth of CNFs. The hierarchical web of ACFs/CNFs was collected for surface characterization and adsorption tests after slowly cooling the reactor and furnace to room temperature. Some samples of Fe-CNFs were also prepared on Fe-ACF(ws). For the reference purpose, such CNF samples are denoted in the manuscript as Fe-CNF(ws).

Fig. 4 describes the tip-growth mechanism of CNFs on Fe-ACFs. There are three mechanistic steps: (1) the decomposition of C6H6 vapor into carbon and hydrogen, which occurs in the active sites of the Fe nanoparticles, (2) the diffusion of the carbon atoms into the metal particles, with the simultaneous escape of H2 from the surface, and (3) the precipitation and crystallization of carbon to form CNFs after it reaches its solubility limit in the Fe nanoparticles. In general, CNFs growth is of two types: tip and base, depending on the interaction (weak or strong) between the metal particles and the ACFs surface. When the interaction is weak, tip-growth is favored. Otherwise, base-growth occurs. The growth of CNFs on metal- (Ni, Cu, and Fe) functionalized ACFs favors mostly the tip-growth mechanism because the interaction is weak. As later corroborated by the SEM images, the growth of CNFs on Fe-ACFs favored the tip-growth mechanism in the present study.

3. Surface characterization

The samples were characterized by several analytical techniques such as atomic absorption spectroscopy (AAS), broad angle X-ray diffraction (XRD), N2-physisorption, H2-chemisorption,
Fourier transform infrared (FT-IR), and scanning electron microscopy (SEM). \( \text{N}_2 \)-physisorption (at 77 K) and \( \text{H}_2 \)-chemisorption were carried out using the Autosorb-1C Quantachrome instrument. XRD patterns were recorded on an X-pert X-ray diffractometer using Cu K\(_\alpha\) radiation (\( k = 1.54178 \text{ Å} \)) within a 2\( \theta \) range of 10° to 80° at a scan rate of 5° per min. FT-IR spectra were recorded on a Tensor 27 (Bruker, Germany) in the wave number range of 400–4000 cm\(^{-1}\) using attenuated total reflectance (ATR) with a germanium (Ge) crystal. The spectra and the corresponding data acquisition were automatically obtained using an interfaced computer and a standard software package. The AAS analysis was carried out by a Varian AA240 using an air-acetylene flame. SEM images were obtained on a field-emission SEM (Supra 40 VP, Zeiss, Germany).

4. Adsorption study for \( \text{CCl}_4 \) removal

Fe-ACFs and Fe-CNFs samples prepared with and without surfactants were used to study the \( \text{CCl}_4 \) removal under flow conditions. The test experimental setup is illustrated in Fig. 5. Briefly, the setup includes the adsorption and gas analysis sections.

The adsorption section consisted of a vertical SS tube (ID = 2.0 mm, \( L = 45 \text{ mm} \)) encapsulated in a SS shell (ID = 15 mm, \( L = 90 \text{ mm} \)) with provisions provided for the gas inlet and outlet. The shell was wrapped with heating tape (1000 W) to maintain a constant temperature with the aid of a PID temperature controller (Fuji Electric Co., Japan). The exit \( \text{CCl}_4 \) concentration from the adsorber was monitored by a gas chromatograph (model 5700, Nucon Eng. Co., India) equipped with a flame ionization detector (FID) and

![Fig. 3. Schematic diagram of horizontal furnace used for calcination, reduction, and CVD.](image)

![Fig. 4. Schematic illustration of CNF Tip-growth mechanism: (a) decomposition of \( \text{C}_6\text{H}_6 \) on and diffusion of carbon species through metal particle, (b) precipitation and formation of CNFs.](image)
5. Results and discussion

5.1. Iron (III) loading on Fe-ACFs

The samples of the Fe(NO₃)₃·9H₂O impregnating solutions were collected for analysis before and after the ACF impregnation, and they were tightly sealed in glass vials. A fixed volume (1 mL) of the solution was then digested for 30 min in 1 mL of nitric acid (HNO₃) and 9 mL of DI water. After digestion, the volume was increased to 10 mL by adding DI water. Next, 10 μL of the sample was pipetted into a 100-μL volumetric stand flask. Samples were quantitatively analyzed for Fe by AAS. A calibration was performed prior to the analysis using the Fe standard solutions supplied by Varian.

Table 1 presents the data for the Fe-ACFs prepared using different surfactants (SDS, TOPO, or Triton X100). For each surfactant, the amount of Fe incorporated into the ACFs was observed to increase with increasing surfactant concentration up to 0.3%. Beyond a 0.3% surfactant concentration, the amount of Fe transferred from the bulk impregnating solution to the ACFs surface considerably decreased.

At relatively higher concentrations, excess surfactants may form micelles that are adsorbed onto the ACFs. The surfactants may also form barriers around the Fe(III) ions because of repulsive forces. These effects may reduce the transfer of Fe(III) ions from the bulk solution to the ACFs surface. Also, the largest Fe loading of approximately 0.4 mg/g was obtained when using SDS. A loading of approximately 0.2 was obtained when using the other surfactants (TOPO and Triton).

5.2. Specific surface area, pore volume, and PSD data

The N₂ adsorption/desorption isotherms at −196 °C were obtained to gain insight into the surface textural properties of various Fe-ACFs samples prepared in this study. All samples were degassed for 8 h at 200 °C under vacuum before the measurement. Figs. 6 and 7 depict the adsorption isotherms for the Fe-ACFs and Fe-CNFs samples, respectively, prepared using different surfactants. As observed, the amount of adsorbed N₂ gradually increased with the pressure relative to the saturation pressure (P/P₀) until P/P₀ = 0.1. Afterward, the amount of adsorbed N₂ became constant, which indicated that the samples were equilibrated with N₂. All adsorption isotherms were Type I according to the BET classification. None of the isotherms showed any significant hysteresis loops, which was indicative of microporosity in the materials.

A sharp increase in the amount of adsorbed N₂ was observed near the saturation pressure for the Fe-CNFs sample prepared using SDS. This increase suggested the presence of narrower pores, or ultramicroporosity, in the sample [43].

The specific surface area of the samples was obtained using the standard BET method over the relative pressure range from 0.05 to 0.35. In this range, the BET equation was assumed to be linear. The total pore volume was calculated from the amount adsorbed at a relative pressure close to unity (i.e., ∼0.994). The meso- and
micropore volumes were obtained using the Barrett–Joyner–Halenda (BJH) and density functional theory (DFT) methods. Both methods were applied using the instrument’s software supplied by Quantachrome.

Table 2 summarizes the data for the BET area and pore volume. There are three salient results. (1) The BET area and pore volume of the Fe-CNFS samples were smaller than those obtained for their substrate (Fe-ACFs). (2) The smallest BET area and pore volume were observed for the Fe-ACFs and Fe-CNFS samples prepared using SDS. (3) The contribution of micropores to the total pore volume was larger than that of the mesopores for all samples except the Fe-CNFS prepared using SDS, which had a larger contribution from the mesopores.

In general, the SBET and pore volume decreased during metal impregnation. However, the area and pore volume increased during calcination and reduction [38]. During impregnation, most of the Fe(III)-surfactant that were transferred from the solution to the ACFs resided in the micropores, which were the larger contributors to the SBET and pore volume. Upon growing CNFs on Fe-ACFs, SBET and pore volume decreased because the pores became narrower. The largest decrease was observed for the ACFs/CNFs samples prepared using SDS, which suggests that SDS promoted the largest transfer of Fe, thus resulting in the largest growth of CNFs. These observations are consistent with the AAS measurements presented in Table 1. The SEM results discussed later in the manuscript corroborate the dense and uniform growth of nanofibers for the Fe-CNFS prepared using SDS. The smallest micropore volume observed for the Fe-CNFS samples prepared using SDS apparently suggests an increase in nanopore content. These pores are not accessible to N2 molecules because of diffusion limitations when using N2 as a probe molecule during the physisorption analysis. Therefore, such measurements are usually underestimated up to approximately 40% [44]. Here, the important point to note is that the BET surface area and micropore volume of Fe-ACF and Fe-CNFS samples prepared using SDS are smaller than those of the other samples, as shown in Table 2.

5.3. H2 chemisorption

The H2 chemisorption study was carried out on the calcined samples of ACFs to determine the metal active surface area (ASA) using the Autosorb–1C instrument. H2 gas was used as an adsorbate molecule. Approximately 0.1 g of the sample was placed in a quartz sample cell. The sample was heated-treated at the rate of 10 K min⁻¹ from room temperature to 473 K and then degassed for 2 h under helium flow at the same temperature. Next, the temperature was increased at the same rate to 673 K, and the sample was further treated for 2 h by H2 at 10 cc min⁻¹ to convert Fe(III) to the pure metallic state, i.e., Fe(0). Next, the sample was cooled under He flow to the analysis temperature (60 °C). The H2 chemisorption analysis was subsequently performed. The ASA (m² Fe per g Fe-ACFs) was calculated by the instrument’s in-built AS-Win software.

Table 3 summarizes the H2 chemisorption analysis data. From the table, it is evident that the largest active Fe surface area was obtained for the Fe-ACFs samples prepared using SDS, which corroborated the previously discussed inference from the present study that SDS enhanced the transfer of Fe(III) ions from the

| Table 2 | Surface area and pore volume analysis of different prepared adsorbent material. |
|---------|---------------------------------|-------------------------------|-----------------|-----------------|-----------------|
| Sample  | SBET (m²/g)                     | Vp (cc/g)                     | Pore volumes (cc/g) |
|         | Micro  | Meso  | Macro  | Micro  | Meso  | Macro  |
| ACFs    | 1386   | 0.8575 | 0.7480 | 0.0681 | 0.0414 |
| Fe-ACFs (ws) | 1286 | 0.7291 | 0.6401 | 0.055  | 0.0340 |
| Fe-ACFSDS | 753  | 0.4198 | 0.3651 | 0.0354 | 0.0193 |
| Fe-ACFSDTOPO | 980  | 0.5372 | 0.4577 | 0.0469 | 0.0252 |
| Fe-ACFTOPO | 1154 | 0.6342 | 0.5200 | 0.065  | 0.0492 |
| Fe-CNFS  | 1054  | 0.5941 | 0.5277 | 0.0601 | 0.0063 |
| Fe-CNFS SDS | 318  | 0.4583 | 0.1324 | 0.3027 | 0.0231 |
| Fe-CNFTOPO | 816  | 0.4635 | 0.3876 | 0.0339 | 0.0418 |
| Fe-CNFTITION | 999  | 0.5775 | 0.4932 | 0.0583 | 0.0259 |

| Table 3 | Chemisorption data of different Fe-ACFs samples prepared at optimum surfactants concentration. |
|---------|----------------------------------------|-----------------|
| Sample name | Name of the surfactant | ASA (m²/g of catalyst) |
| ACFs | ws | 0.3160 |
| Fe-ACFs | SDS | 0.6874 |
|          | TOP2 | 0.3437 |
|          | TRITON | 0.1936 |
impregnating solution to the ACFs surface because of strong interactions between the anionic SDS and cationic Fe(III) ions. As observed from the table, the ASA was measured to be 0.713 m² g⁻¹ for the Fe-ACFs sample prepared using SDS. Based on the ASA, the rank among the samples was SDS > TOPO > Triton X100 > without surfactant. In fact, there was a marginal increase in the ASA of the samples prepared using TOPO surfactants and a considerable decrease in the ASA of the samples prepared using Triton surfactants.

5.4. FT-IR analysis

The FT-IR spectrum was recorded for the Fe-ACFs samples before and after CCl₄ adsorption. During the measurement, the sample chamber was continuously purged with N₂ to minimize the effect of atmospheric carbon dioxide and moisture. The background spectrum was recorded prior to recording the sample spectra. A total of 100 scans were collected for each sample. The resolution was set to 4 cm⁻¹. An atmospheric compensation algorithm was applied to reduce the atmospheric interference in the sample chamber.

Fig. 8 shows the representative FT-IR spectra. Differences in the functional groups of the samples (before and after adsorption) were observed. The peak at ~600 cm⁻¹ in the spent sample corresponds to the C-Cl stretch of alkyl halides. An enhancement in the peak intensity was observed because of −Cl incorporation on the ACFs surface. Similarly, the peak at ~1000 cm⁻¹ in the spent sample is attributed to the C=O stretch of the carbonyl group, which was also enhanced after adsorption. Also, the peak intensities of CO₂ and the carbonyl groups at around 2300 cm⁻¹ and ~3600 cm⁻¹, respectively, were enhanced following adsorption.

5.5. Surface morphology

Fig. 9a contains the SEM image of Fe-ACF prepared as a substrate for growing CNFs. The Fe-nanoparticles may be observed on the surface and in the pores. Fig. 9b contains the SEM images of the Fe-CNPs, which were grown on Fe-ACFs by CCVD. The images shown in Fig. 9b are at small (5 KX) and large (200 KX) magnifications for each sample (Fe-CNPs, Fe-CNFSDS, Fe-CNFTOP, and Fe-CNFTRITON). The corresponding scales shown on the images are in µm for small magnifications and nm for large magnifications.

The Fe-CNFSDS sample (Fig. 9b b-b') exhibited a uniform surface with dense growth compared to the Fe-CNPs sample (Fig. 9b a-a').

In addition, the uniformity of the CNFs growth on the Fe-CNFSDS sample was superior to that on the Fe-CNFTRITON (Fig. 9b c-c') and Fe-CNFTOP samples. The Fe-CNFTRITON samples exhibited a small CNF yield and a low uniformity. Also, the fibers of the Fe-CNFSDS samples were thinner than those of the other samples, which was attributed to the relatively small size of the Fe crystals on the Fe-ACFSDS samples.

5.6. XRD spectra

The XRD patterns of the Fe-ACFs samples prepared with and without surfactants are shown in Fig. 10. For comparison, the XRD spectrum of the as-received ACFs sample was also recorded. As expected, no Fe peaks were observed in the as-received ACFs sample. However, one characteristic peak for Fe nanoparticles was observed at 2θ= 44.6°, and the other shoulder peak was observed at 65°, which corresponds to the crystallographic indices of the (110) and (200) planes, respectively. The patterns confirm that the prepared samples contained Fe in its pure metallic FCC phase. A common peak was also observed at around 22° (2θ) for all the samples, which is characteristic of amorphous carbon having a crystallographic index of (002). It can be observed from the figure that the peak at 44.6° was the sharpest for the Fe-ACFTRITON samples, followed by the Fe-ACFs, Fe-ACFSDS, and Fe-ACFTOP samples.

The size of Fe particles in the Fe-ACFs samples was calculated using the Scherrer formula and was found to be 17 nm. The size drastically decreased to 8 nm for the Fe-CNFSDS samples. Therefore, we infer that the surfactant helped to control the size of the Fe nanoparticles. In addition, the anionic SDS yielded the smallest crystals, which was facilitated by the monodispersion of Fe(III) ions in the impregnating solution, as previously mentioned in the manuscript. The average crystal sizes for the Fe-ACFs, Fe-ACFSDS, Fe-ACFTOP, and Fe-ACFTRITON samples were calculated to be 17, 8, 12, and 16 nm, respectively. The results are consistent with the AAS data previously described. Therefore, it may also be concluded from the analysis of the XRD data, together with the SEM images, that the small Fe nanoparticles prepared using SDS helped in producing dense and uniform CNFs.

5.7. CCl₄ removal

Fig. 11 shows the adsorption breakthrough curves for CCl₄ on Fe-ACFs. The breakthrough analysis was carried out to evaluate the performance of the prepared adsorbents. As observed from the figure, the Fe-CNFSDS samples exhibited superior adsorption behavior compared to the other samples under identical experimental conditions, with the breakthrough and saturation times observed for the Fe-CNFSDS samples being larger than those for the Fe-ACFs samples prepared either with TOPO, with Triton X-100, or without surfactant. The breakthrough time and saturation times were defined as the time to reach ~1% and ~99%, respectively, of the CCl₄ concentration at the inlet to the tubular adsorber. Fig. 12 describes the breakthrough curves for different Fe-CNPs samples.

As observed, the adsorption performance of the samples was found to be similar to that of the Fe-ACFs samples, and the samples ranked in breakthrough and saturation times as follows: Fe-CNFSDS > Fe-ACFTOP > Fe-ACF > Fe-ACFTRITON. Note that the samples prepared using SDS exhibited the largest breakthrough and saturation times. Table 4 summarizes the equilibrium loading (mg analyte per g adsorbent) obtained for different materials. The loading (analyte uptake) was calculated from the breakthrough curve by determining the area above the curve and performing a mass balance under flow conditions [39]. As shown, the calculated CCl₄ loading for the different adsorbents is ranked in the same order as mentioned above.
Fig. 9. (a) SEM image of Fe-ACFs prepared as a substrate for growing CNFs. (b) SEM images of Fe-CNFs prepared without surfactant (a, a’) and using different surfactants: SDS (b, b’), TOPO (c, c’), and Triton (d, d’).
Fig. 10. XRD patterns of different Fe-ACF samples.

Fig. 11. Breakthrough curves for the adsorption of CCl₄ over different Fe-ACFs (W = 1 g, Q = 0.2 slpm, T = 50 °C, Cᵢ₀ = 3000 ppm).

Table 4

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<th>Sample name</th>
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6. Conclusions

A method was developed to prepare Fe-ACFs and Fe-CNfs using SDS, an anionic surfactant. The Fe-ACFs prepared using SDS were used to prepare an adsorbent for VOC removal. The Fe-ACFs were also used as a substrate to grow CNFs by CVD. The surface characterization data and the adsorption results show that the surfactant-mediated transfer of Fe(III) ions from the impregnating solution to the ACFs surface, and the subsequent in situ production of Fe nanoparticles by the calcination of the transferred Fe(III)-SDS on ACFs followed by reduction, is an attractive method to develop Fe-ACFs and then grow CNFs on the Fe-ACFs. The method promoted the enhanced transfer of Fe(III) ions to the ACFs, and eventually, the monodispersity of Fe nanoparticles on the ACFs. The yield and uniformity of the CNFs were relatively larger using SDS. The prepared Fe-ACF(3) and Fe-CNFS(3) samples were shown to be effective adsorbents for VOC removal.

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