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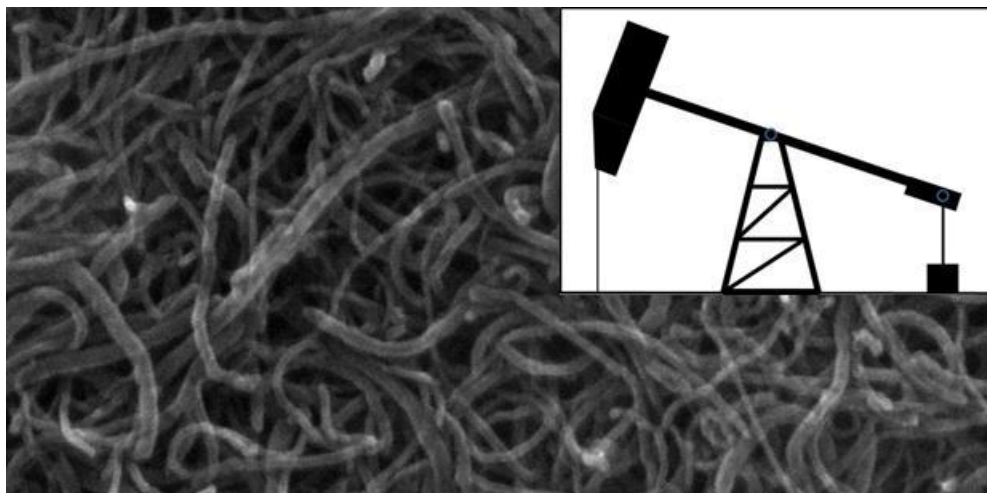
An assessment of muti-walled CNTs as a sorbent for the health-risk-driving BTEX compounds in oilfield produced water.

Impact Statement

A major environmental challenge associated with oilfield operations is the handling of large volumes of co-extracted produced water, which upon untreated discharge, can impact ecological receptors and drinking water resources. Granular activated carbon is typically used for dissolved organics removal from produced water but is considered difficult to regenerate. The thermal stability and electrical conductivity of carbon-based nanomaterials makes them suitable as potential regenerable sorbents. In this study, multi-walled carbon nanotubes (MWNTs) were evaluated as sorbents for the removal of environmental risk-driving BTEX compounds from low and high salinity produced water in the presence of other dissolved hydrocarbons. To the best of our knowledge, there is no past work on the treatment of dissolved phase produced water using carbon nanotubes.

ES:P&I

Environmental Science: Processes & Impacts

Sustainable Solutions and Technologies

Using multi-walled carbon nanotubes (MWNTs) for oilfield produced water treatment to environmentally acceptable endpoints

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In this study, multi-walled carbon nanotubes (MWNTs) were employed to remove benzene, toluene, ethylbenzene, and xylenes (BTEX) from low and high salinity waters pre-equilibrated with crude oil. The treatment endpoint of crude oil-contaminated water is often controlled by BTEX compounds owing to their higher aqueous solubility and human-health toxicity compared to other hydrocarbons. The MWNTs sorbent was extensively characterized and the depletion of organic sorbate from the produced waters was monitored by gas
10 chromatography-mass spectrometry (GC-MS) and total organic carbon (TOC) analyses. The equilibrium sorptive removal of BTEX followed the order: ethylbenzene/ *o*-xylene > *m*-xylene > toluene > benzene in the presence of other competing organics in produced water. Sorption mechanisms were explored through the application of a variety of kinetics and equilibrium models. Pseudo 2nd order kinetics and Freundlich equilibrium models were best at describing BTEX removal from produced water. Hydrophobic interactions between the MWNTs and BTEX, as well as the physical characteristics of the sorbate molecules, were regarded as primary factors
15 responsible for regulating competitive adsorption. Salinity played a critical role in limiting sorptive removal, with BTEX and total organic carbon (TOC) removal falling by 27% and 25%, respectively, upon the introduction of saline conditions. Results suggest MWNTs are effective at removing risk-driving BTEX compounds from low-salinity oilfield produced waters.

Introduction

20   A major environmental challenge associated with petroleum exploration and production (E&P) is the handling of large volumes of water co-extracted during these operations [1]. This so-called "produced water" exists in equilibrium with oil in petroleum reservoirs, and its global daily production is estimated
25 to be over 200 million barrels, which is about three times higher than daily oil production [2]. Produced water has a wide range of chemical constituents, including petroleum hydrocarbons, electrolytes, heavy metals, and radionuclides [3]. The chemical composition of produced water can vary considerably between
30 different oil fields and geological formations with respect to its dissolved organic content and its salinity, which can range from brackish to hypersaline [2, 4]. Practical environmental options for the handling of produced water include re-injection back into the petroleum-bearing reservoir for enhanced oil recovery (EOR),
35 and post-treatment reuse or disposal [5].

   The potential environmental impacts of produced water discharge are an increasing cause of concern because toxic organic compounds, such as particular aromatic hydrocarbons and phenols, can occur in significant concentrations in produced
40 water. These compounds can bioaccumulate in marine animals upon discharge of produced water into aquatic ecosystems [6], or impact drinking water resources. Total polyaromatic hydrocarbons (PAHs) and high molecular weight alkylphenols in untreated produced water occur at concentrations ranging from
45 about 0.040 to 3 mg/L. The concentrations of BTEX in produced water range from 68 to 600,000 μg/L [6, 7]. The level of benzene in produced water, for instance, has been reported above 35,000 μg/L, which is over 7,000 folds higher than the regulatory standards for drinking water (5 μg/L) in the US [7]. The high
50 solubility is due to the high affinity of BTEX compounds for water [7]. Hence, there is a critical need for the adequate treatment of produced water prior to environmental discharge.

   Typically, the only parameter regulated for produced water discharge is its oil and grease (O&G) content. However, the
55 discharge limit of this parameter in treated produced water varies among countries. An average allowable O&G limit for the discharge of treated produced water is 42 mg/L in the US, while it is only 30 mg/L in Australia [2] . In addition, a "No Discharge" requirement remains in place for coastal oil and gas facilities in
60 the US, stemming from a concern over the BTEX, naphthalene, and phenol content of produced water [8].

   A number of physical, chemical, and biological methods have been proposed for the treatment of the organic content of produced water. Some of these methods include de-oiling,
65 chemical oxidation, adsorption, sand filtration, cyclone separation, chemical precipitation, membrane-based separation, photocatalysis, electrodialysis, and trickling filters [2, 9]. More specifically, the removal of dissolved organics in produced water involves the use of granular activated carbon (GAC), air
70 stripping, centrifugal flotation systems, and surfactant-modified alumino-silicate materials like zeolites for BTEX removal [6, 10].

   The application of nanomaterials presents various advantages over conventional technologies owing to their unique characteristics. Carbon based nanomaterials are among the most
75 widely used nanomaterials for environmental applications [11-15]. Amongst others, some of the desired properties of carbon based nanomaterials are: (1) large surface area, (2) high intra-particle diffusion, (3) high surface reactivity, and (4) regenerative properties [12, 13, 16, 17]. Most recently, phase-separated oil has been
80 demonstrated to be recovered from water using carbon nanotube sponges [18]. However, to the best of our knowledge, there is no past work in literature on the treatment of produced water from crude oil E&P using carbon nanotubes.

   The objective of this study was to evaluate the effectiveness
85 of multiwalled carbon nanotubes (MWNTs) as sorbents for the treatment of dissolved hydrocarbons in produced water, with a

special emphasis on the risk-driving BTEX compounds, which often determine treatment endpoints for petroleum-contaminated waters. In order to better reflect real-world scenarios of produced water treatment, BTEX removal was assessed in the presence of the remaining dissolved hydrocarbon mixture emanating from crude oil. Both freshwater and saline water saturated with crude oil hydrocarbons were tested to differentiate produced water treatment from the treatment of freshwater contaminated with crude oil. MWNTs were selected for this study over other carbonaceous nanomaterials owing to their bigger market share [19], lower cost [20], easier bulk production [20], and decreased cytotoxicity [21] when compared with single walled carbon nanotubes.

Materials and methods

Materials

Alkane analytical standard (C8–C20), NaCl, KHCO$_3$, CaCO$_3$, and MgCl$_2$.6H$_2$O were purchased from Sigma-Aldrich® (Steinheim, Germany). HC BTEX mix standard (benzene, toluene, ethyl benzene, o-, m-, p-xylene) was purchased from Supelco, Sigma-Aldrich® (Steinheim, Germany). Milli-Q water (~18.2 MΩ.cm) was used throughout the study. MWNTs were purchased from Cheaptubes, Inc., (Brattleboro, VT, USA). The manufacturer reported MWNTs as over 99% mass/mass plasma purified dry powder. The specific surface area and electrical conductivity of the MWNTs was at least 233 m^2/g and 100 S/cm, respectively. Also, according to the manufacturer, the outer diameter of MWNTs was between 13-18 nm and their lengths ranged from 1 to 12 μm. Crude oil from the onshore Asab oilfield located in the Emirate of Abu Dhabi [22] was provided by the Abu Dhabi Company for Onshore Oil Operations (ADCO) in a sealed container with almost no headspace. The container was stored under ambient conditions. Asab crude is a sweet light crude with an API gravity of 40.7° (reported in 1993) [22]. Pure Asab crude oil sample comprised of the C6 to C34 aliphatic hydrocarbons, BTEX, naphthalene and other aromatic hydrocarbon derivatives, whereby the identities of the compounds were confirmed by mass spectral library matching to the Wiley-NIST library during gas chromatography – mass spectrometry (GC-MS) analysis.

Characterization of MWNTs

Electron Microscopy: The structure of MWNTs was examined by scanning electron microscopy using an FEI Quanta FEG 250 SEM from FEI Co. (Hillsboro, OR, USA). The equipment was operated at ~5-30 keV. Prior to imaging, the MWNTs surface was coated with <50 nm layer of gold and palladium using a GATAN Model 682 precision etching coating system (PECS). Energy Dispersive Spectroscopy (EDS) was employed to determine the elemental composition of MWNTs. TEAM software was used for this purpose.

BET surface area: BET surface area of MWNTs was measured by NOVA 2200e automated gas sorption system (Quantachrome, FL., USA) using nitrogen gas at 77 K. The data was analyzed by Quantachrome NovaWin Data Acquisition and Reduction software version 11.02, provided by the manufacturer. The adsorption/desorption isotherms of N$_2$ was measured at a relative pressure (P/P$_0$), ranging from 0.0001 to 0.99. The Brunauer, Emmett and Teller (BET) equation was utilized to determine the specific surface area.

Aggregate size and Surface charge measurements: The aggregate size and surface charge of MWNTs were measured at 23±1 °C using a ZetaPALS analyzer from Brookhaven Instruments Corp., (Holtsville, NY, USA). Dynamic light scattering (DLS) technique was used to estimate aggregate size of MWNTs. The DLS and zeta potential measurements were performed by varying pH and conductivity of the background solution. The details of zeta potential measurements can be found elsewhere [13]. Prior to particulate size and zeta potential measurements, the MWNTs were suspended in water with the aid of ultrasonication. A bath sonicator was used for ultrasonication together with an established protocol [17] to obtain stable suspensions.

Synthesis of produced water

Deionized (Milli-Q) water and salt-enriched Milli-Q water were used for generating produced water by equilibrating them with Asab crude oil using the following procedures.

Deionized produced water (DI-PW): The Asab crude oil was mixed with ultra-pure Milli-Q water in an amber bottle in a 1:10 ratio by volume. The mixture was kept in sealed bottle with no headspace to avoid the vaporization of volatile compounds present therein. The water-crude oil mixture was stirred for 2 hours using a magnetic stirrer and transferred to 500-mL borosilicate separatory funnels. After an equilibration time of 24 hours, the produced water was collected in a 1-liter glass bottle for later experimentation with MWNTs. Additionally; two 40ml samples of the produced water were collected for BTEX analysis and total organic carbon (TOC) measurements as described in section 2.4.

Salt enriched produced water (SE-PW): Salt enriched produced water was synthesized according to the reported composition [2, 23] by adding weighed amount of the salts mentioned in the Materials section in 1L of deionized water to produce the following: 68 mEq/L sodium (Na$^+$), 3 mEq/L potassium (K$^+$), 31 mEq/L calcium (Ca^{2+}), 3 mEq/L magnesium (Mg^{2+}), 116 mEq/L bicarbonate (HCO^{3-}), 2 mEq/L carbonate (CO$_3^{2-}$) and 4 mEq/L chloride (Cl$^-$) ions. The mixed salt solution had a salinity of 9615 mg/L. The mixture was continuously stirred for 24 hours. Afterwards, the salt enriched water was mixed with the Asab crude oil sample and equilibrated as described earlier. The salt-enriched produced water was collected for GC-MS and TOC analysis and, for experimentation with MWNTs.

Analysis of produced water

TOC measurement: TOC content of the solution was measured before and after treatment of the non-saline and saline hydrocarbon-containing waters with MWNTs. Samples were collected in 40-ml sterile glass vials and loaded on a Sievers InnovOx® Laboratory TOC analyzer (GE, Colorado, USA) connected to an autosampler. The equipment uses supercritical water oxidation, which ensures efficient oxidation irrespective of sample impurities and produces higher accuracy in TOC measurement. Each 40-ml sample was analyzed six times to assess the precision in the measurement of mean measured TOC values.

BTEX composition: Aqueous dissolved benzene, toluene, ethylbenzene, and xylenes (BTEX) composition was determined by GC-MS. Dissolved volatile constituents in the samples were pre-concentrated using a Teledyne Tekmar purge-and-trap concentrator (PTC, v 11/09, Teledyne Technologies, USA) interfaced with an Agilent gas chromatograph and single quadrupole mass spectrometer detector (Agilent 7890GC/ 5975MSD, Agilent Technologies, USA). The temperature program involved a 5 minute hold time at 35 °C, temperature ramping at 10 °C /min to 320 °C, and a final holding time of 15 minutes. GC injector was operated in the splitless mode and mass spectral matching was performed from full scans against a Wiley/NIST library. A spectral match above 95% was obtained for all target BTEX compounds in the sample.
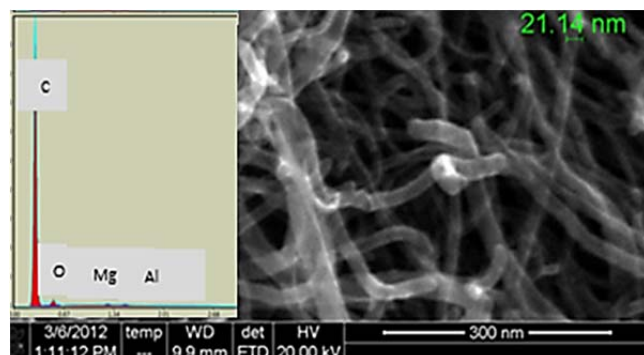
Fig. 1 Scanning electron micrograph and EDX of MWNTs.

The MS was operated in the selected ion mode (SIM) for quantitation of the BTEX compounds. Target ion mass-to-charge (m/z) ratios were used for the quantitation of benzene (78.0), toluene (91.0), ethyl benzene (91.0) and xylene (91.0).

Other aromatic compounds: In addition to the BTEX compounds, the following 4 aromatic compounds were detected in the produced water samples: (1) ethylmethylbenzene, (2) trimethylbenzene, (3) 1,2,3-trimethylbenzene, and (4) naphthalene. The GC-MS analytical method described above was used for the detection of these compounds. Spectral library match was used for the confirmation of the presence of these compounds in the samples. Quantitation was carried out using the average response factor of the n-alkane fraction marker (>C8-C10) because all 4 compounds eluted at retention times that were within the bounds of this fraction.

Adsorption experiments

A stock solution of 1000 mg/L of MWNTs was prepared by adding 400 mg of MWNTs to 400 mL of deionized water and mixing the suspension over magnetic stirring. The MWNTs were not subjected to additional treatment such as chemical functionalization or ultrasonication, in order to accurately replicate the use of MWNTs in potential commercial produced water treatment applications. The batch experiments were performed to understand kinetics and estimate equilibrium concentrations in MWNTs-produced water systems. 40 mL of produced water was acquired in each amber glass vial from stock, which was previously stored at 4°C in air-tight container with virtually no headspace. Then small volumes of stabilized MWNTs stock solution were added to these vials to achieve desired concentrations of MWNTs in produced water. The headspace in the vials was minimized by appropriately filling and sealing the vials with Teflon lined septa. The samples were then stirred using a multi-shaker (Model FMS 3, FINE PCR, Seoul, Korea) operated between 50 and 60 Hz. Prior to GC-MS analysis, the samples were filtered through GF/C filter papers from Millipore Corp. (Billerica, MA, USA) using a manual syringe filtration system. The manual syringe filtration system consisted of glass syringe filter fitted with stainless steel EMD Millipore™ Microsyringe Filter Holder. The filtrate was collected in 10 mL air tight vials from Dionex Corp. (Sunnyvale, CA, USA). The vials were sealed and stored at 4°C until analysis. All the adsorption experiments were performed at room temperature (23 ± 1 °C) and in triplicate.

The kinetics and equilibrium uptake of BTEX by MWNTs was calculated by the following equations, respectively:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

where, q_t (mg/L) is the solid phase concentration of BTEX constituents at time, t (hrs). C_0 (mg/L) and C_t (mg/L) are the liquid-phase concentrations of BTEX at time t= 0 hrs and t= t hrs, respectively. V (L) is the volume of solution and m (g) is the mass of MWNTs. q_e (mg/L) and C_e (mg/L) are the respective solid and liquid phase concentrations of BTEX constituents at equilibrium.

3. Results and discussion
Characterization of MWNTs

SEM micrographs were used to study the morphological structure of MWNTs. The outer diameter of individual MWNT was approximately 21 nm as shown in Fig. 1. However, the MWNTs usually exist in the form of aggregates in aqueous systems unless suspended using chemical or physical methods [17]. The EDX analysis revealed the presence of metallic impurities (like magnesium and aluminum) in MWNTs as shown in the insert of Fig. 1.

These impurities were also reported by the manufacturer. Nitrogen adsorption/desorption for MWNTs were determined by N_2 adsorption isotherm measured at 77 K, the results of which can be seen in Fig. 2a. The BET adsorption isotherm obtained was type IV and, therefore, similar to earlier observed one of the similar material [24]. The BET surface area of our MWNTs was also comparable with the previously reported theoretical [25] and experimental [24, 26] values. The effect of pH on aggregation of MWNTs is presented in Fig. 2b. The pH range was selected from 5 to10, which is typical of oilfield produced waters [2]. The average diameter of MWNTs aggregates ranged from 600-1500 nm. From SEM observations (Fig. 1) and DLS data (Fig.2b), it can be inferred that 50 ± 20 MWNTs aggregated together to form a cluster through a pH range of 5 to10. The zeta potential of our MWNTs was -40 mV to -22 mV. The detailed description of the surface charge of similar material can be found elsewhere [13].
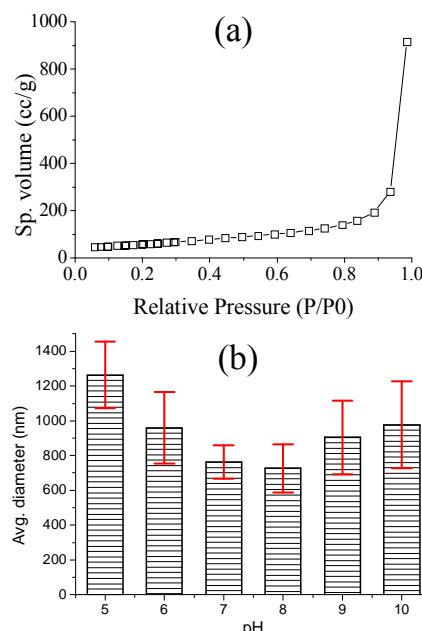

Fig. 2 (a) Adsorption/desorption of nitrogen on MWNTs at 77K. (b) Aggregate size of MWNTs agglomerates in water at various pH. obtained by dynamic light scattering.

Table 1: Concentration of compounds (up to C10) in produced water before and after treatment with MWNTs. The equilibrium was reached after 72hrs of contact time.

Compound	DI-PW		SE-PW		Quanti-tation method
	Initial conc. (mg/L)	Eq. conc (mg/L)	Initial conc. (mg/L)	Eq. conc (mg/L)	
Benzene	9.74 ±0.21	5.90 ±0.31	9.97 ±0.64	7.22 ±0.53	Standards
Toluene	11.62 ±0.73	4.84 ±1.50	12.05 ±0.57	9.12 ±0.99	
Ethylbenzene	11.50 ±1.29	2.30 ±0.81	11.73 ±1.14	8.07 ±1.01	
o-xylene	12.01 ±0.77	4.19 ±1.25	12.35 ±0.53	6.52 ±0.21	
m-xylene	11.29 ±0.14	3.53 ±0.92	11.47 ±0.70	6.52 ±0.21	
ETMB	56.48 ±0.93	36.10 ±1.34	61.24 ±0.61	51.19 ±0.98	
TMB	22.61 ±1.04	12.89 ±0.63	30.06 ±1.07	22.20 ±0.22	
1,2,3TMB	24.48 ±0.87	20.34 ±0.93	27.18 ±0.66	23.78 ±0.27	
Naphthalene	25.42 ±0.75	16.85 ±0.75	24.80 ±0.78	21.79 ±0.97	Fractional markers
TOC	18.71 ±10.5	5.89 ±3.67	5.16 ±3.83	2.92 ± 1.67	TOC Analyzer

Key: Ethylbenzene (ETB); Ethylmethylbenzene (ETMB or EMB); Trimethylbenzene (TMB); Total Organic Carbon (TOC).

Gas chromatography-mass spectroscopy (GC-MS)

The aqueous concentrations of key organic compounds, as well as the total organic carbon, in DI-PW and SE-PW initially and after equilibrium with MWNTs are tabulated in Table 1. The values in Table 1 represent the effectiveness of MWNTs in adsorbing organics from DI-PW and SE-PW. The extent of adsorption of organic compounds on MWNTs varies widely, depending upon the background solution (DI-PW or SE-PW) and type of adsorbing organic molecule. The ethylbenzene in DI-PW showed highest removal by adsorption (~70%), whereas, naphthalene in SE-PW was minimally removed (~12%) by MWNTs at equilibrium. Fig.3. shows the total ion current (TIC) chromatographs of major compounds in produced water before and after treatment with MWNTs (50 mg/L). The complex mixture of organics in produced water is evident from the chromatographs in Fig. 3a. The BTEX peak height counts in Fig. 3a were very high (~2.8e7 to 4e7) when compared to other dissolved organics in produced water. These peak heights, as well as the total number of peaks representing the wide range of compounds, significantly decreased after treatment of produced water with MWNTs. The peaks of octanol, nonane, decane, undecane, and dodecane were also not significant after treatment. The comparison of chromatographs, before and after treatment with MWNTs, suggests the ability of MWNTs to remove BTEX and other organics from produced water. Therefore, adsorption kinetics studies were performed to understand the adsorption mechanism.

TOC adsorption on MWNTs

At equilibrium, MWNTs (50 mg/L) effectively sorb TOC from DI-PW (68.5%) and SE-PW (43.3%) which can be seen in Table 1. TOC is the primary constituent of produced water (67-38,000 mg/L) [2], therefore, appears to be the biggest competitor for the adsorption sites present on MWNTs. The TOC is not a direct indicator of toxicity but it may significantly reduce the effectiveness of sorbent (MWNTs) to remove BTEX by occupying the limited sorption sites. The TOC removal by MWNTs decreased by 25% upon increasing the salinity of

produced water from DI-PW to SE-PW. The decreased adsorption of TOC in the presence of high concentration of background ions (i.e. SE-PW) is not compatible with the previous observations where activated carbon was used as a sorbent [27], indicating perhaps that the MWNT sorbent's characteristics change with salinity [28].
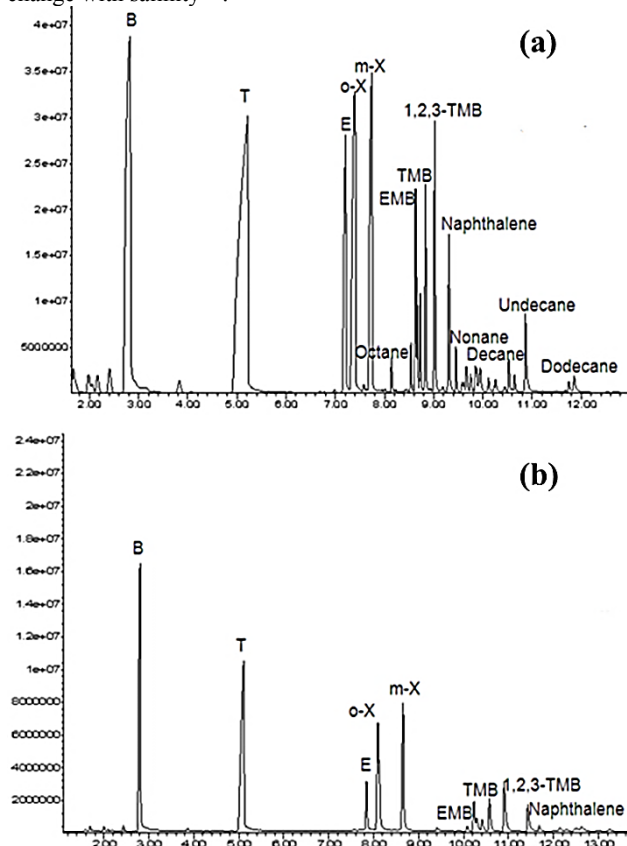

Fig. 3 Comparison of representative chromatograms of produced water samples before (a) and after (b) treatment with MWNTs (50 mg/L) at equilibrium. Aliphatic fractions present in the produced water sample were almost completely removed, while a reduction was observed in the concentration of the BTEX compounds post-treatment with MWNTs. *Key: o-X (ortho-xylene), m-X (meta- xylene), EMB (ethylmethylbenzene), TMB (trimethylbenzene, 1,2,4- & 1,3,5-), 1,2,3-TMB (1,2,3- TMB).*

BTEX adsorption kinetics

The adsorption kinetics tests were carried out at a maximum of 120 hrs while keeping a constant MWNTs concentration of 50 mg/L. Fig. 4 presents the results from adsorption kinetics experiments. The equilibrium was reached after a maximum of 24 hrs for benzene, toluene, ethylbenzene, and o-xylene, whereas m-xylene required ~72 hrs to reach a state of equilibrium. Adsorption kinetics were observed for another 48 hrs (120 hrs in total) to establish the equilibrium time and to evidence desorption, if any.

Fig. 4 (a1 and a2) depict the adsorption of BTEX from DI-PW onto MWNTs over time. Fig. 4 (a1) describes the whole range of adsorption kinetics from 0 to 120 hrs, while the initial adsorption kinetics (≤ 4hrs) can be seen in Fig. 4 (a2). The initial order of adsorption, at the end of a 30-minute contact time, on MWNTs was: toluene (34.6 mg/g-MWNTs) > o-xylene (31.2 mg/g-MWNTs) > benzene (20.6 mg/g-MWNTs) > m-xylene (10.8 mg/g-MWNTs) > ethylbenzene (3.6 mg/g-MWNTs). However, this order changed to ethylbenzene > o-xylene > toluene > m-xylene > benzene after 4hrs contact time. Finally, after 120 hrs of contact, the cumulative adsorption was:
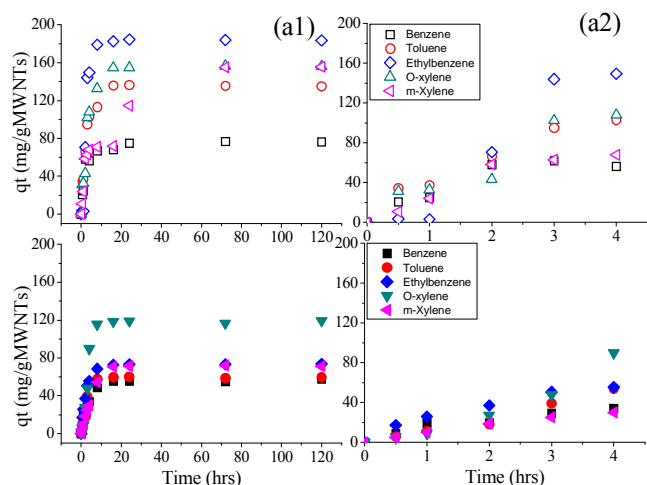
Fig. 4 Adsorption of BTEX on MWNTs in DI-PW from (a1) 0 - 120 hrs and (a2) 0 - 4 hrs. In SE-PW from (b1) 0 - 120 hrs and (b2) 0 - 4 hrs.

ethylbenzene (183.4 mg/g-MWNTs) > o-xylene (156 mg/g-MWNTs) > m-xylene (155.6 mg/g-MWNTs) > toluene (135 mg/g-MWNTs) > benzene (70 mg/g-MWNTs).

Fig. 4 (b1 and b2) present the adsorption of BTEX from SE-PW onto MWNTs over time. Fig. 4 (b1) shows the adsorption kinetics from 0 to 120 hrs and Fig. 4 (b2) represents the initial adsorption kinetics (≤ 4hrs). Contrary to the BTEX removal trend observed for DI-PW, ethylbenzene took the lead in adsorbing onto MWNTs, initially, followed by benzene, toluene, o-xylene, and m-xylene, respectively. After 30 min contact time, 17.2, 8.8, 5.8, 5.6, and 4.8 mg/g of ethylbenzene, benzene, toluene, o-xylene, and m-xylene were removed. This adsorption order changed to o-xylene > ethylbenzene > toluene > benzene > m-xylene in next 4 hrs. Finally after 120 hrs, 119.2 mg/g o-xylene, 73.4 mg/g ethylbenzene, 71.2 mg/g m-xylene, 59.4 mg/g toluene, and 57.8 mg/g benzene were removed from the system. It is clear from the Fig. 4 that the sorptive removal of BTEX from SE-PW was always lower than from DI-PW, indicating that produced water salinity, which varies considerably by oil-bearing formation, is an impeding factor in attaining BTEX removal using MWNTs.

This erratic adsorption behavior of BTEX on MWNTs in DI-PW and SE-PW lead to a more in-depth investigation into adsorption kinetics. As stated earlier, our DLS results (Fig. 2b) and SEM (Fig. 1) observations suggest MWNT aggregates of approximately 30-70 tubes. In general, the MWNT aggregates can have two major adsorption areas: (1) surface of MWNTs bundle including grooves, and (2) interstitial spaces between MWNTs bundle. Therefore, BTEX adsorption on MWNTs can be divided into surface and intra-particle adsorption. The surface adsorption was tested using Pseudo 1st and 2nd order kinetic models, whereas, the intra-particle adsorption was analyzed by the Weber and Morris model [14, 29]. The adsorption kinetic models fitted to the experimental data are presented in Table 2, while the values of experimental equilibrium concentrations ($q_{e,exp}$), calculated equilibrium concentrations ($q_{e,cal}$), rate constants (k_1, k_2, and k_{ip}), correlation coefficients (R^2), and other parameters [(1/b)ln(ab, 1/b, and Ci)] are listed in Table 3 (Pseudo 1st order, Pseudo 2nd order kinetic, and Intra-particle diffusion model).

The linear form of Langergren and Svenska definition of Pseudo 1st order sorption kinetics model [29], plot of ln ($q_e - q_t$) vs t, gives the slope of k_1 and intercept of ln q_e (Fig. S1). Table 3 shows the disagreement between calculated and experimental solid phase equilibrium concentrations for the Pseudo 1st order

kinetics, in most cases. However, toluene (DI-PW), ethylbenzene (SE-PW), and m-xylene (SE-PW) adsorption on MWNTs follow the Pseudo 1st order kinetics with high regression coefficient (≥ 0.98) (Table 3). The differences between experimental and the (Pseudo 1st order kinetic model) predicted equilibrium concentrations of toluene (DI-PW), ethylbenzene (SE-PW), and m-xylene (SE-PW) were 2.23%, 5.13%, and 0.79%, respectively.

Pseudo 2nd order kinetic model is widely reported to describe adsorption of organics on MWNTs [24, 30, 31]. Table 2 illustrates the good agreement between the experimental and calculated values of q_e obtained from the linear plot of $\frac{t}{q}$ vs t (Fig. 5), except ethylbenzene (DI-PW). Also, the values of regression coefficient are nearly unity which signifies the applicability of Pseudo 2nd order kinetic model to describe the adsorption process of BTEX from DI-PW and SE-PW onto MWNTs.

Since Pseudo 1st and 2nd order kinetic models did not identify the diffusion of BTEX into MWNTs aggregates, therefore, the adsorption mechanism can be explored through the application of intra-particle diffusion model (Table 2). The model was proposed by Weber and Morris, and is based on Fick's second law [29, 32]. It can be studied by plotting q_t versus $t^{1/2}$, the intercept of which gives an idea about the boundary layer thickness (the larger the intercept, the higher the boundary layer effect) and whether intra-particle diffusion is the rate limiting step. Also, if the plot is linear and passes through the origin, the Intra-particle diffusion will be the rate limiting step [29]. The adsorption process is controlled by intra-particle adsorption if the plot produces a single straight line [24], while multiple linear plots are indicative of additional controlling parameters [24, 29]. Fig. 6 represents the intra-particle diffusion model fittings to the experimental dataset which is a mixture of single and two-step straight lines. The fitting parameters can be found in Table 3.

From Fig. 6 and Table 3, it can be concluded that the o-xylene and m-xylene were adsorbed onto MWNTs in a single step and intra-particle diffusion was likely the only controlling parameter. Conversely, the adsorption of benzene, toluene, and ethylbenzene was affected by other parameters as well [24]. In the case of DI-PW, benzene and toluene required 3hrs and ethylbenzene required 8hrs to adsorb on the external surface of MWNTs (from aqueous solution) before diffusing inside the MWNTs aggregates, whereas, o-xylene and m-xylene never traveled into the interstitial spaces inside the MWNTs bundles.
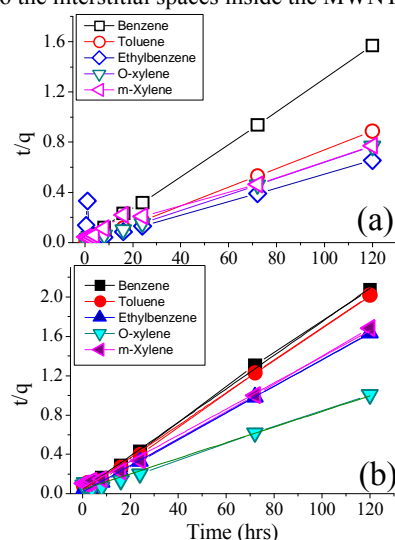

Fig. 5 Pseudo 2nd order kinetics for the adsorption of BTEX on MWNTs in (a) DI-PW and (b) SE-PW.

Table 2: Mathematical expressions and nomenclature for the adsorption models fitted for the BTEX adsorption on MWNTs.

Adsorption model	Mathematical expression	Nomenclature		
Pseudo 1st order	$\ln(q_e - q_t) = \ln q_e - k_1 . t$	q_e	mg/L	Amount of adsorbate adsorbed at equilibrium
		q_t	mg/L	Amount of adsorbate adsorbed at time ,t
		k_1	1/hr	Pseudo 1st order rate constant
		t	hr	Time
Pseudo 2nd order	$\dfrac{t}{q} = \dfrac{1}{k_2 . q_e^2} + \left(\dfrac{t}{q_e}\right)$	k_2	g/ (mg. h)	Pseudo 2nd order rate constant
Intra-particle	$q_t = k_{pi} t^{1/2} + C_i$	k_{pi}	mg/ (g.h$^{1/2}$)	Rate parameter
		C_i		Thickness of boundary layer
Langmuir Isotherm	$q_e = \dfrac{Q_0 K_L Ce}{1 + K_L Ce}$	Q_0	mg/g	Maximum adsorption capacity
		K_L	L/mg	Langmuir fitting parameter
		Ce	mg/L	Equilibrium solution phase concentration
Freundlich Isotherm	$q_e = K_f Ce^{1/n}$	K_f	(mg/g)/ (mg/L)$^{(1/n)}$	Freundlich affinity coefficient
		n		Dimensionless number

Table 3: Pseudo 1st order, Pseudo 2nd order, and Intra-particle kinetic constants and correlation coefficients for the adsorption of BTEX on MWNTs

	Pseudo 1st order				Pseudo 2nd order			Step 1 (Intra-particle)				Step 2 (Intra-particle)		
DI-PW														
	$q_{e\ exp}$	$q_{e,\ cal}$	k_1	R^2	$q_{e,\ cal}$	k_2	R^2	T_1 (hr)	k_{p1}	C_1	R_1^2	k_{p2}	C_2	R_2^2
Benzene	76.8	65.91	0.40	0.7801	77.46	0.01	1.00	3	38.14	-3.94	0.94	2.37	57.55	0.92
Toluene	135.6	132.57	0.36	0.9807	137.55	0.01	1.00	3	52.41	-4.2	0.96	4.66	96.54	0.96
Ethylbenzene	184	231.13	0.48	0.9124	216.45	0.00	0.74	8	74.12	-16.15	0.9	0.05	183	0.05
o-Xylene	156.4	160.32	0.30	0.9078	160.00	0.00	1.00	16	41.5	-16.15	0.9	N/A*	N/A	N/A
m-Xylene	155.2	150.61	0.16	0.919	166.11	0.00	0.98	72	18.4	9.42	0.92	N/A	N/A	N/A
SE-PW														
Benzene	55	51.60	0.23	0.96	58.58	0.01	1.00	8	17.32	-1.24	0.98	0.37	53.75	1
Toluene	58.6	77.96	0.57	0.8491	60.75	0.01	1.00	8	22.07	-6.15	0.93	0.667	56.93	1
Ethylbenzene	73.2	69.44	0.35	0.9905	74.40	0.01	1.00	8	25.51	1.08	0.98	72.32	72.35	0.86
o-Xylene	116.6	139.34	0.33	0.8223	125.94	0.00	0.99	16	31.89	-12.45	0.96	N/A	N/A	N/A
m-Xylene	72	71.43	0.14	0.9959	75.30	0.00	1.00	24	16.94	-3.39	0.96	N/A	N/A	N/A

* N/A = Not applicable because of the one step adsorption of xylenes on MWNTs.

Similar adsorption phenomena were observed in SE-PW except for the longer surface adsorption time for benzene and toluene (which increased from 3hrs to 8hrs). This slow film diffusion can be attributed to increased ion complexation in SE-PW. The rapid adsorption of benzene and toluene and their traveling into the interstitial spaces of MWNTs aggregates might be due to their smaller molecular radii and low molecular weights when compared to xylenes [33].

Hydrophobic interactions between BTEX and MWNTs can be another explanation of the preferred adsorption of xylenes and ethylbenzene when compared to benzene and toluene. The log Kow values of BTEX constituents are: benzene (2.13), toluene (2.73), ethylbenzene (3.15), o-xylene (3.12), and m-xylene (3.2). The relatively less hydrophobic molecules of benzene and toluene have comparatively lower adsorption on hydrophobic MWNTs compared to ethylbenzene and xylenes. Once the adsorption of BTEX on MWNTs reached equilibrium, the widely accepted adsorption models were fitted to the experimental data in order to verify the complexity of adsorption phenomena in our studied system.

BTEX adsorption isotherms

Fig. S1 and S2 show the adsorption of BTEX on MWNTs in the presence of DI-PW and SE-PW, until it reaches equilibrium. Linearized Langmuir (Fig. S1) and Freundlich (Fig. S2) isotherms were used to fit the sorption data. The details of these equilibrium models can be found in Table 2. Table 4 lists the fitting parameters of the isotherms investigated. Adsorption of organics on MWNTs is frequently reported to follow Langmuir and Freundlich adsorption models [34-36]. Conceptually, the

Langmuir isotherm assumes a single-layer adsorption with limited sorption sites, whereas the Freundlich isotherm describes multilayer adsorption. In single layer adsorption process, the adsorbate molecules only interact with adsorbate surface throughout the adsorption process, however, in multilayer adsorption, the adsorbate molecules initially interact with adsorbent surface and then with each other [16].
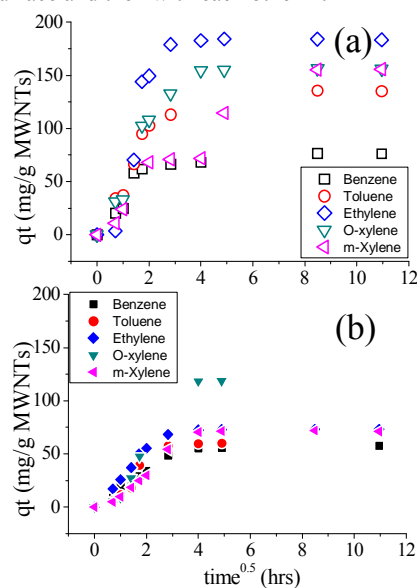

Fig. 6 Plot of intra-particle diffusion model for the adsorption of BTEX on MWNTs in (a) DI-PW and (b) SE-PW.

Table 4 suggests that the adsorption in this study could not be explained by Langmuir isotherm model because of negative values of Q_0 and K_L. However, Freundlich isotherm model explains the adsorption very well. Log K_f values for DI-PW were always higher than that of SE-PW which signifies the decreased adsorption of BTEX on MWNTs in the presence of high concentration of background ions (SE-PW). Also, the correlation coefficient values of Freundlich isotherms applied on DI-PW system are comparatively higher than that of SE-PW (except m-xylene where they are equal i.e. 0.99). Therefore, adsorption of BTEX on MWNTs in produced water must be a multilayer adsorption where BTEX molecules first adsorbed on MWNTs and then interacted with each other to reach the state of adsorption equilibrium.

Table 4 Equilibrium isotherm model constants and correlation coefficients for the adsorption of BTEX on MWNTs.

	Langmuir			Freundlich		
	DI-PW					
	Q_0	K_L	R^2	K_f	n	R^2
Benzene	-68.87	-0.12	0.83	1.05	0.339	0.98
Toluene	-88.89	-0.14	0.79	1.10	0.294	0.97
Ethylbenzene	-222.22	-0.16	0.87	22.76	0.469	0.96
o-Xylene	-113.77	-0.15	0.71	2.33	0.318	0.94
m-Xylene	-85.69	-0.18	0.85	1.63	0.274	0.99
	SE-PW					
Benzene	-63.29	-0.08	0.87	1.024	0.436	0.95
Toluene	-84.03	-0.07	0.68	1.011	0.455	0.91
Ethylbenzene	-79.37	-0.05	0.67	1.142	0.535	0.90
o-Xylene	-102.04	-0.08	0.76	1.263	0.425	0.92
m-Xylene	-92.59	-0.08	0.98	1.366	0.436	0.99

Conclusions

Despite comparable initial BTEX concentrations in DI-PW and SE-PW, the salinity played a significant role in determining the extent of BTEX removal by MWNTs in part due to its effects on MWNT sorbent's characteristics. BTEX removal decreased by 27% (on average) in SE-PW as compared to DI-PW, comparable to the concomitant 25% decrease in adsorption of TOC from DI-PW to SE-PW. The adsorption removal of benzene, toluene, ethylbenzene, o-xylene, and m-xylene was reduced by 12%, 34%, 49%,18%, and 26%, respectively, in the presence of salt in produced water (i.e. in SE-PW). Pseudo 2nd order kinetics and Freundlich equilibrium models described the adsorption of BTEX on MWNTs in produced water. At equilibrium, the removal of BTEX was in the following order: DI-PW: ethylbenzene > o-xylene > m-xylene > toluene > benzene, and SE-PE: o-xylene > ethylbenzene > m-xylene > toluene > benzene. Based on an analysis of sorption kinetics in oilfield produced water, ethylbenzene, o-xylene, and m-xylene only adsorbed on the surface of MWNTs aggregates, whereas, benzene and toluene diffused inside the interstitial spaces probably due to their comparatively smaller sizes. Results indicate that MWNTs have the potential to remove dissolved organics, including BTEX, from oilfield produced water. However, salinity of the produced water, which can vary considerably from reservoir to reservoir, can limit BTEX removal. Removal of BTEX and other hydrocarbons from produced water following thermal or chemical regeneration of the MWNTs sorbent remains to be explored.

Notes and references

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