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Characterizing toluene adsorption onto carbon nanotubes for environmental applications

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ABSTRACT

Two different types of carbon nanotubes (CNTs), multi-walled and single-walled carbon nanotubes (MWCNTs and SWCNTs, respectively), have been characterized as new potential sorbents for contaminant removal from aqueous phase and can be used through different technological implementations. The performance of the materials has been evaluated in comparison with the most commonly used carbonaceous material, activated carbon (AC). Adsorption properties were evaluated by kinetic and equilibrium batch tests in aqueous solution at different salinity levels. Toluene was chosen as the reference compound to simulate the water phase dissolved portion of an oil spill. The experimental results have clearly demonstrated faster motion and higher adsorption capacity of MWCNTs and SWCNTs compared with AC. CNTs have shown very high removal efficiency for dissolved toluene, up to 30% and 90% for MWCNTs and SWCNTs, respectively. These results are very promising for the prospective use of CNTs as a potential alternative sorbent for hydrophobic organic compound (HOC) removal in environmental applications.

Keywords: Isotherm; Kinetic; Adsorption; Carbonaceous materials; Carbon nanotubes

1. Introduction

Adsorption techniques are largely used for remediation purposes to remove a wide range of contaminants, from heavy metals [1] to organic compounds [2]. Carbonaceous materials have been largely investigated as sorbents to remove contaminants from different environmental matrices, such as contaminated groundwater and wastewater [3,4], but also from sediments such as active amendment [5,6]. Their high sorption efficiency is mostly due to their large exposed surface area. To extend the application of the adsorption processes for environmental purposes, several sorbents, both synthetic and natural, have been considered and characterized by the scientific community.

In this work, two different types of carbon nanotubes (CNTs) have been characterized in comparison with the more common carbonaceous material, activated carbon (AC) [7], as new potential sorbents that could be used in contaminant removal from aqueous phase through different technological implementations. This study is integrated in the frame of Kill Spill, a European-funded project aimed to develop highly efficient, economically and environmentally viable (bio)technological solutions for the cleanup of oil spills caused by maritime transport or offshore oil exploration and related processes. Several conventional strategies for oil spill cleanup

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involve the use of sorbent materials. Indeed, sorbent materials can be used in booms to remove floating organic fraction or as amendment to in situ immobilize high-molecular-weight organic compounds in the sediments. Several sorbents are able to remove the separate phase but are often inadequate to sorb the dissolved contamination. In this regard, the characterization of sorbents able to remove contaminants dissolved in aqueous phase is therefore a demanding environmental issue.

CNTs are composed of rolled-up graphene sheets. MWCNTs have multiple graphene sheets, whereas SWCNTs are composed of a single graphene shell [8]. CNT diameters range from 0.4 nm to 3 nm for single-walled CNTs, whereas multi-walled diameters range from 1.4 nm to 100 nm [9]. Primary means of CNT synthesis include chemical vapor deposition (CVD) [10] and a catalytic method using metal and metal oxide [11]. Several minerals were used as natural catalysts for MWCNT synthesis, such as bentonite [12], alumina [13], volcanic rock and red soil [14]. In the literature, CNTs have been used for H_2 storage and for biosensor fabrication [15] or for their electrical and conductive components, in fact the introduction of CNTs into a polymeric matrix improves the electric conductivity of the polymer [16].

CNTs have been already considered as sorbent materials for environmental applications [17–20]. Upadhyayula et al. [21] reported the efficiency of CNTs in the field of wastewater treatment: high sorption capacity was shown for the nanotubes' fibrous shape due to their large external surface area that is available for contaminant adsorption [22]. CNT application is increasing because they can be easily functionalized via sidewall surface modification by covalent or non-covalent functionalization [21]. CNT functionalization can be a useful tool for extending the range of contaminants, such as metals [23] and organic compounds [24], that could be adsorbed, but they can also represent a valuable method for increasing the nanotube dispersibility in water solution [15]. CNTs have also been used in environmental application as nanostructured reactive membranes for water treatment and desalination [15]. The main disadvantage of using CNTs in environmental applications may be their toxicity and their uptake in unicellular protozoa [25]. Nevertheless, significant progress has been made to make CNTs biocompatible materials [26,27]; many studies are aiming at this purpose, for example, by adding hydroxyl, carboxyl and amine groups to increase their solubility and especially their biocompatibility [15]. Moreover, Wu et al. [28] reported a method to generate biocompatible CNTs by using a bioactive coating to mitigate their toxicity; this may be very convenient in the prospective use of CNTs for environmental applications.

Two types of CNTs, multi-walled and single-walled carbon nanotubes (MWCNTs and SWCNTs, respectively), were characterized in aqueous solutions at different levels of salinity; toluene was chosen as a target hydrophobic organic compound (HOC) dissolved in aqueous phase. Toluene is one of the more mobile, available and soluble HOCs among the oil constituents and is capable of directly indicating the behavior of benzene, ethylbenzene and xylene, but it can also be used to extrapolate the behavior of the more hydrophobic oil components including long-chain alkanes and polycyclic aromatic hydrocarbons. Adsorption properties were evaluated by kinetic and equilibrium batch tests in aqueous solution; different salinity conditions, ranging from pure to synthetic seawater, were investigated to assess the possible applicability of the tested materials under real conditions.

2. Materials and methods

2.1. Sorbent materials

The AC Norit, type Darco®, was purchased from Sigma-Aldrich®. This AC is derived from lignite coal. It is a granular material, and as pretreatment AC was sieved to a size range of 0.5–1 mm. The AC is characterized by a high surface area (650 $m^2 g^{-1}$, as reported in the Sigma-Aldrich® technical sheet) and a total pore volume of 0.9 $mL g^{-1}$.

MWCNTs were purchased from CheapTubes® (Vermont, USA). These MWCNTs have an outer diameter of 50–80 nm, inner diameter of 5–10 nm, length of 10–20 μm, ash content less than 1.5 wt%, purity higher than 95 wt% and specific surface area of 60 $m^2 g^{-1}$.

Single-walled CNTs were bought from CheapTubes®, and their characteristics are described as follows. The SWCNTs have a diameter of 1–2 nm, average length of 3–30 μm, purity higher than 99 wt%, ash amount of 0 wt% and specific surface area of approximately 400 $m^2 g^{-1}$. No preliminary steps were carried out for CNT materials. All materials were stored in a desiccator to avoid water adsorption.

2.2. Batch configuration

2.2.1. Kinetic tests

Batch configuration was chosen for comparing the material behavior under different conditions. Kinetic and equilibrium tests were carried out in deionized water and synthetic seawater to compare material performance under a range of conditions. To simulate seawater composition, Sigma-Aldrich® sea salt was used. Sea salt is an artificial salt mixture closely resembling the composition of the dissolved salts in ocean water; 40 $g L^{-1}$ of sea salt was dissolved in deionized water to carry out the seawater experiments.

Monocomponent solutions of the target hydrophobic organic pollutant—that is, toluene—were used to evaluate the adsorption properties of each sorbent material: AC, MWCNTs and SWCNTs. Toluene was spiked in deionized water to obtain concentrated solution at approximately 350 $mg L^{-1}$, and the system was left in a closed glass bottle under magnetic stirring for 24 h. After 24 h, the toluene was completely dissolved (toluene solubility is 535 $mg L^{-1}$ [29]), and the inoculated solution was put in a Tedlar bag (5 L) to avoid any volatilization in headspace and stored at 25°C (room temperature). For the experimental tests, glass vials sealed by a Teflon face gray butyl stopper (Wheaton, Millville, NJ) and crimped by an aluminum cap were used. An aliquot of concentrated toluene solution was sampled from the Tedlar bag by glass syringe and spiked to the glass vials where the sorbent material was placed. No headspace was left in the vial to avoid any toluene volatilization. Toluene was dissolved in water solution (no toluene was presented as a separate phase). Kinetic and equilibrium tests were carried out under magnetic stirring at 15 revolutions per minute (RPM); the batches were furthermore kept at room temperature of 25°C for the duration of all tests.

Kinetic tests were performed to evaluate the equilibrium time needed for the isotherm tests but also to compare the material performance. Different solid/liquid ratios were adopted for the experimental tests due to the different sorptive capacities: 0.02 L of contaminated solution was placed in contact with 0.02 g of sorbent materials (AC and MWCNTs) for a sorbent-solution ratio of approximately 1 g L^{-1}; 0.010 mL of contaminated solution was placed put in contact with 0.0015 g of SWCNTs for a sorbent-solution ratio of approximately 0.15 g L^{-1}.

An aliquot of the solution was sampled from the liquid phase at the test beginning ($t = 0$) to evaluate the starting dissolved concentration (C_0) of toluene; the other samples were collected after the fixed times: 0.25, 0.5, 1, 2, 3, 4, 5, 6, and 7 h. An aliquot of the solution was sampled from the aqueous media after 24 h to evaluate the equilibrium achievement.

2.2.2. Equilibrium tests

For the equilibrium tests (isotherms), the same experimental kinetic tests setup was adopted; an aliquot of aqueous solution was sampled at the test start ($t = 0$) for evaluating the toluene initial concentration C_0, and C_e was determined after 24 h. Based on the previous kinetic study, 24 h was considered to be sufficient for equilibrium achievement. The equilibrium sorbed concentration q_e, expressed in mg g^{-1}, was calculated by the following equation (Eq. (1)):

$$q_e = \frac{(C_0 - C_e)V}{w} \tag{1}$$

where C_0 is the starting toluene concentration expressed in mg L^{-1}; q_e is the toluene sorbed amount (mg g^{-1}); C_e is the equilibrium toluene concentration expressed in mg L^{-1}; V is the solution volume expressed in liters and w is the sorbent material weight expressed in grams. The equilibrium tests were carried out while maintaining a constant sorbent-solution ratio and changing the initial toluene concentration.

2.3. Analytical method

2.3.1. Gas chromatography (GC)

The toluene headspace concentration was determined by gas chromatography (DANI GC 1000 equipped with a DANI 86.50 headspace autosampler, Milan, IT) using a capillary column (75 m length, 0.53 mm ID, TRB 624) and a flame ionization detector (FID). For headspace analysis, a 100-µL sample was diluted with 3 mL of deionized water and sealed in a 10-mL headspace vial fitted with a Teflon-faced butyl septum. Sample injection was operated in splitless mode, where the injector temperature was set at 180°C. The carrier gas (He) flow was 14 mL min^{-1}. The oven program temperature was as follows: 60°C for 0.5 min increasing at 6°C min^{-1} to 110°C for 0 min then increasing at 15°C min^{-1} to 180°C for 0 min. The headspace sampler analysis conditions are reported as follows: oven temperature 70°C, manifold temperature 75°C, transfer line temperature 180°C, shaking soft. Toluene was detected using a FID as previously reported. Air and H_2 were used for FID, and their flow rates were 1.1 and 0.65 mL min^{-1}, respectively. The detector temperature was 250°C. The GC was previously calibrated with standard toluene concentrations over a linear response range.

2.3.2. SEM

A Zeiss Auriga FESEM (Field Emission Scanning Electron Microscope) has been used. Scanning electron microscopy (SEM) analysis was performed to evaluate the morphology of the materials. The analyses were performed on the as-received materials (without any pretreatment).

2.4. Modeling and calculation

2.4.1. Kinetic modeling

Kinetic experimental data were fitted according to a mathematical model developed for toluene adsorption by using Micromath® Scientist 1.0 for parameter optimization. Toluene adsorption was represented by an aspecific interaction mechanism between dissolved toluene and active sorbent surface. The adsorption kinetic expression was described by the pseudo- first-order equation, as reported below (Eq. (2)):

$$\frac{dq_t}{dt} = k(q_e - q_t) \tag{2}$$

where k is the adsorption kinetic constant (h^{-1}); q_e is the equilibrium sorbed toluene concentration expressed in mg g^{-1}; and q_t is the sorbed toluene concentration at time t as calculated by using Eq. (3):

$$q_t = (C_0 - C_t)V / w \tag{3}$$

where C_0 and C_t are the toluene concentration at time 0 (initial toluene concentration) and the toluene concentration at time t expressed in mg L^{-1}, respectively; V is the volume of the liquid phase (L); and w is the sorbent amount expressed in grams.

The model assumes a negligible external transport, due to the high turbulence given by the stirring condition, and represents the motion linearly dependent on the adsorption driving force (given by the difference between q_e and q_t). Integrating Eq. (2) between $q_t = 0$ and q_t and between 0 and t, the kinetic equation for toluene adsorption becomes:

$$q = q_e - q_e * e^{-kt} \tag{4}$$

Optimization of k and q_e have been obtained by non-linear regression of q_t vs. t experimental data according to model (4).

2.4.2. Equilibrium modeling

Isotherm equilibrium tests have been carried out to investigate the adsorption behavior of the different materials and their affinity for the selected contaminant. Exothermic physical interactions (Van der Waals and London forces) are responsible for the removal of the organic molecules on the sorbent surface.

It must be specified that the thermodynamic modeling (isotherm) was performed only for comparison purposes.

Thus, no specific physical meaning has been attributed to the optimized parameters. Three isotherm models were used to fit the experimental equilibrium data: the linear, Langmuir and Freundlich isotherm models. The models have been applied to each experimental plot to evaluate which one better simulates the material adsorption behavior; the linear, Freundlich and Langmuir models are reported below according to Eqs. 5, 6 and 7, respectively:

$$q_e = KC_e \quad (5)$$

$$q_e = K_F C_e^n \quad (6)$$

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \quad (7)$$

where q_e (mg g^{-1}) is the equilibrium sorbed concentration; K is the linear thermodynamic constant expressed in L g^{-1} and C_e (mg L^{-1}) is the equilibrium dissolved concentration in the liquid phase. The Freundlich constant K_F is expressed in L g^{-1}, and n is a dimensionless parameter greater than zero; $n > 1$ indicates upwards concavity, whereas $n < 1$ represents downwards concavity. Usually, n is an empirical parameter, although some authors have given it a physical meaning considering it as a measure of the surface heterogeneity [30]. The maximum adsorbable amount, $q_{\max}$, is expressed in mg g^{-1}, whereas K_L is the Langmuir constant expressed in L mg^{-1}.

3. Results and discussion

3.1. SEM analyses

SEM analyses were carried out to characterize the morphology of the CNT samples. In Figs. 1(a)–(e), MWCNT images with magnifications of 30,000× (Fig. 1(a)) and 150,000× (Figs. 1(b) and (c)) and SWCNT images with magnifications 130,000× (Fig. 1(d)) and 200,000× (Fig. 1(e)) are shown. MWCNTs appear as tangles comprising nanotubes whose range of diameters is in agreement with the specifications of the manufacturer. No other forms of carbon were detected. In the case of SWCNTs, the morphology of the sample is more difficult to analyze, considering also that the specifications given by the manufacturer for this material are at the limits of the spatial resolution of the instrument. The material appears as undefined agglomerates from which filaments with diameters of a few nanometers emerge. These filaments are almost certainly SWCNT bundles that exit from agglomerates made of the bundles themselves. This hypothesis is supported by a characterization of the same material by High-resolution transmission electron microscopy (HR-TEM) reported in the literature [31] in which also no other forms of carbon were detected, as in the case of MWCNTs.

3.2. Kinetic tests

Toluene kinetic experimental results obtained in deionized water on AC, MWCNTs and SWCNTs are reported in Figs. 2(a)–(c) along with the simulated model predicted behavior. As shown in Fig. 2, all tests are satisfactorily represented by the adopted kinetic model (4); this is also confirmed by the high calculated regression coefficients (R^2) and correlation values as reported in Table 1. Both MWCNTs and

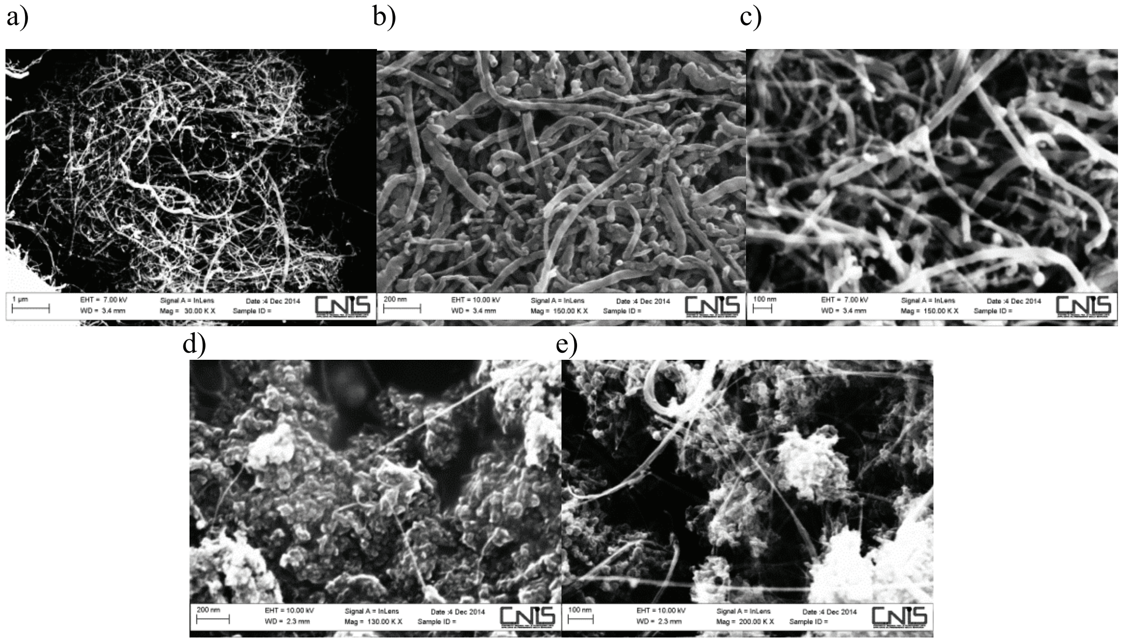

Fig. 1. SEM images: (a) MWCNT SEM image 1 µm, (b) MWCNT SEM image 200 nm, (c) MWCNT SEM image 100 nm, (d) SWCNT SEM image 200 nm and (e) SWCNT SEM image 100 nm.

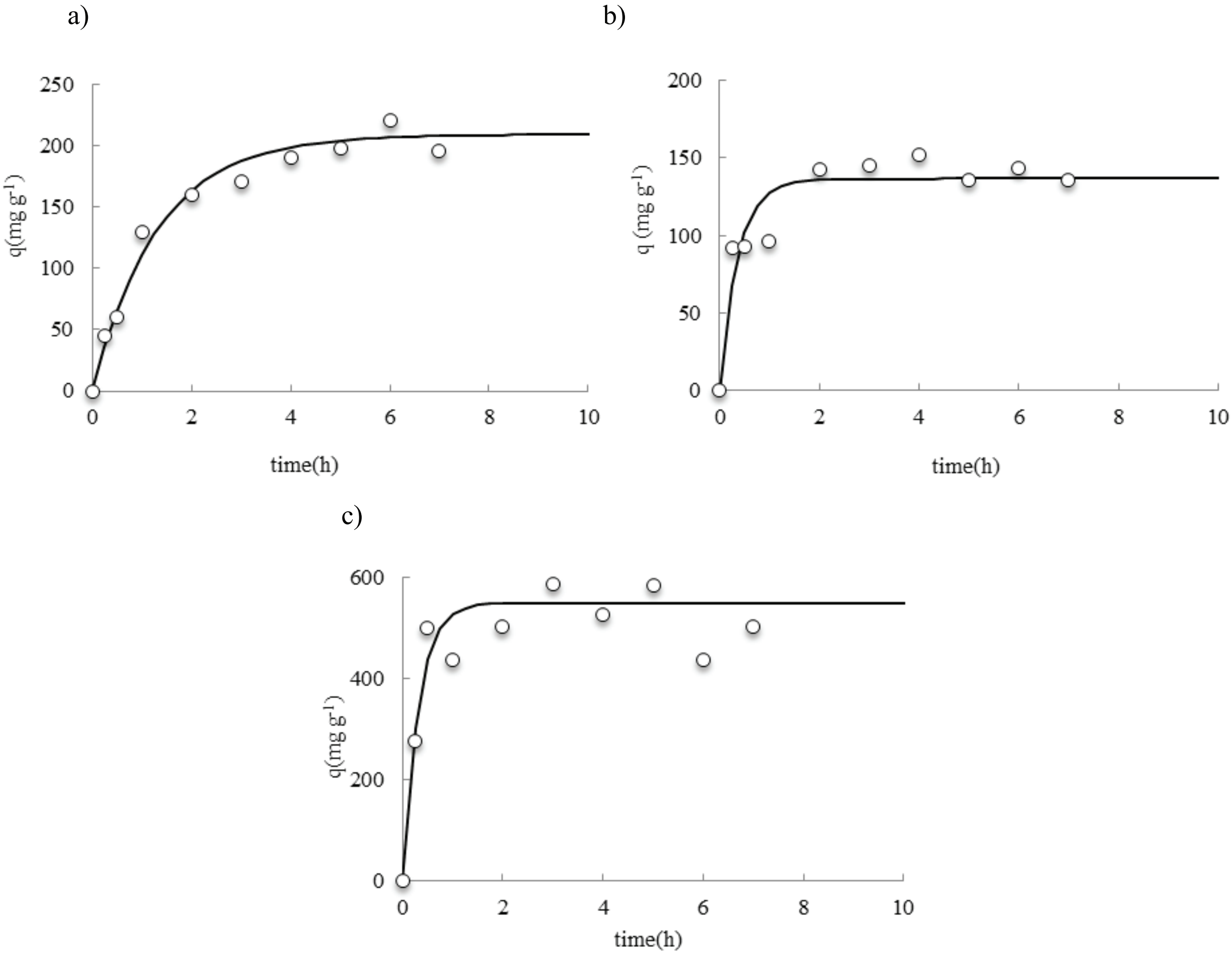

Fig. 2. Toluene kinetic tests in deionized water. Experimental data vs. model calculation: (a) activated carbon, (b) multi-walled carbon nanotubes and (c) single-walled carbon nanotubes.

Table 1
Adsorption kinetic constant, equilibrium sorbed concentration, regression coefficient factor and correlation parameters for kinetic tests in deionized and synthetic seawater

	AC	MWCNTs	SWCNTs
Deionized water			
q_e (mg g^{-1})	209 ± 6.81	137 ± 5.81	550 ± 33.6
k (h^{-1})	0.755 ± 0.0982	2.72 ± 0.651	3.17 ± 1.15
R^2	0.994	0.987	0.972
Correlation	0.987	0.943	0.893
Seawater			
q_e (mg g^{-1})	136 ± 5.42	166 ± 3.47	602 ± 24.9
k (h^{-1})	0.856 ± 0.143	9.12 ± 2.51	3.61 ± 0.932
R^2	0.991	0.997	0.987
Correlation	0.977	0.964	0.943

SWCNTs are characterized by a faster adsorption kinetic than AC. Indeed, 2–3 h was sufficient to achieve equilibrium condition for CNTs, whereas 5–6 h was needed to reach the toluene equilibrium concentration with AC. These considerations are also quantitatively derivable from the comparison of optimized k values for the different sorbent materials (Table 1). Besides, the adsorption kinetic typically depends on the accessibility of the sorbent surface. Adsorption onto AC occurs mostly inside internal porosity, after kinetically limited molecular diffusion of the contaminant. On the other hand, toluene uptake occurs faster onto CNTs where diffusion processes are negligible.

The potential effect of the ionic strength on toluene adsorption kinetics has been evaluated by tests carried out in synthetic seawater solution, and the experimental results are reported in Figs. 3(a)–(c). In addition, in this case, the kinetic model satisfactorily represented the experimental behavior in the entire experimental range, thus allowing the parameter comparison. The optimized values for k and q_e are reported for all tested materials in Table 1. CNT kinetics are still faster than AC kinetics. Moreover, all k values increase with respect to the corresponding values obtained in deionized water

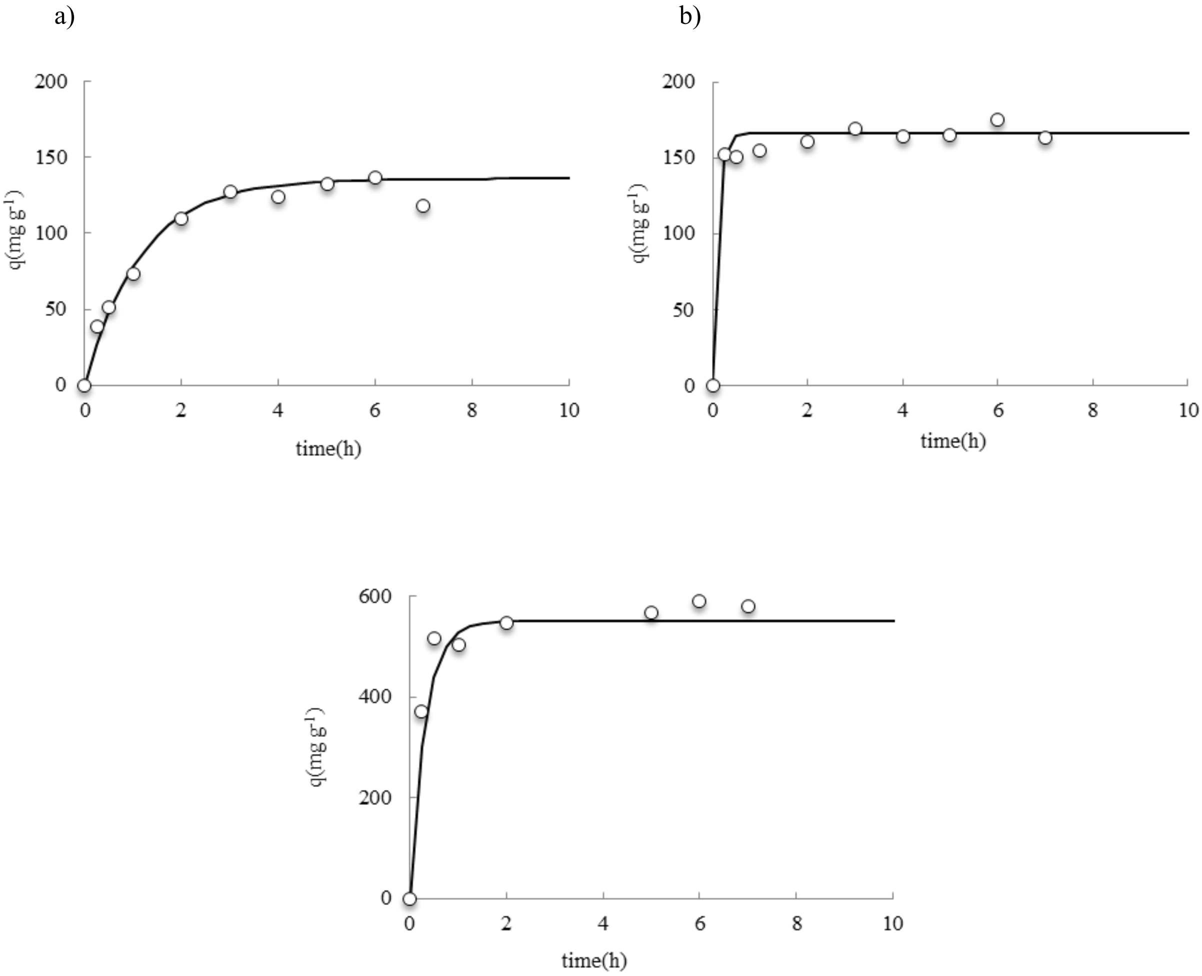

Fig. 3. Toluene kinetic tests in synthetic seawater. Experimental data vs. model calculation: (a) activated carbon, (b) multi-walled carbon nanotubes and (c) single-walled carbon nanotubes.

solution. Toluene is a HOC whose solubility in water is quite low [29], so seawater represents a less affine solution for the toluene with the respect to deionized water. By this regard, water solution with high salt content (seawater) could cause toluene and HOCs to be more rapidly sorbed onto the sorbent material surface. MWCNTs have shown the most significant increase. This aspect is more evident with CNTs because of their significantly higher hydrophobicity with respect to AC.

3.3. Equilibrium tests

AC data have been represented by using the Freundlich and Langmuir models. The linear model was not considered in this case because AC data clearly show that the adsorbed amount of toluene does not linearly increase with increasing toluene dissolved concentration, and a downward concavity is indeed evident. Table 2 reports the parameter optimized values, the regression coefficients R^2 and the correlation factors for the Langmuir and Freundlich models. Experimental data are well fitted by both Langmuir and Freundlich. This dual behavior has already been reported for organic contaminant adsorption onto AC surfaces, although the Freundlich model is the most common for modeling AC equilibrium tests [3,32]. Freundlich fitting is often more representative than that of Langmuir because of its specific applicability. The Langmuir isotherm is based on strict assumptions such as a continuous monolayer of contaminants sorbed onto a homogeneous solid surface and a homogeneous adsorption energy. The Freundlich model assumes that the overlapping of several sorption phenomena occurring at different sites involves a non-homogeneous site energy that can result.

MWCNT experimental sorption data have been modeled by using the Freundlich and linear models. The Langmuir model has not been considered for modeling toluene adsorption onto MWCNTs because the upwards concavity of the experimental data disagrees with the Langmuir type shape. Table 2 reports the optimized parameter values, the regression coefficients R^2 and the correlation factors for both models. As shown in Table 2, both models well fit the toluene adsorption experimental isotherm onto MWCNTs.

SWCNT equilibrium adsorption data were modeled with the Freundlich and linear models; the Langmuir isotherm was excluded considering the absence of an experimental plateau. Both models similarly fit adsorption data as indicated

Table 2
Isotherm optimized parameters, regression coefficients and correlation factors for kinetic tests in deionized and synthetic seawater

		AC	MWCNTs	SWCNTs
Deionized water				
Linear				
	K (L g^{-1})	n.d.	0.515 ± 0.0322	2.94 ± 0.103
	R^2	n.d.	0.952	0.992
	Correlation	n.d.	0.924	0.978
Freundlich				
	K_F (L g^{-1})	40.2 ± 5.07	$7.29 \times 10^{-3} \pm 7.53 \times 10^{-3}$	2.49 ± 1.71
	n	0.237 ± 0.0284	1.77 ± 0.182	1.03 ± 0.124
	R^2	0.995	0.980	0.992
	Correlation	0.965	0.970	0.978
Langmuir				
	$q_{\max}$ (mg g^{-1})	136 ± 8.16	n.d.	n.d.
	K_L (L mg^{-1})	$8.56 \times 10^{-2} \pm 2.58 \times 10^{-2}$	n.d.	n.d.
	R^2	0.991	n.d.	n.d.
	Correlation	0.939	n.d.	n.d.
Seawater				
Linear				
	K (L g^{-1})	n.d.	0.808 ± 0.0640	3.32 ± 0.139
	R^2	n.d.	0.935	0.988
	Correlation	n.d.	0.913	0.981
Freundlich				
	K_F (L g^{-1})	39.6 ± 6.41	$4.23 \times 10^{-3} \pm 6.73 \times 10^{-3}$	1.36 ± 0.962
	n	0.295 ± 0.0388	1.98 ± 0.293	1.17 ± 0.137
	R^2	0.977	0.971	0.991
	Correlation	0.909	0.954	0.983
Langmuir				
	$q_{\max}$ (mg g^{-1})	166 ± 10.4	n.d.	n.d.
	K_L (L mg^{-1})	$8.59 \times 10^{-2} \pm 2.31 \times 10^{-2}$	n.d.	n.d.
	R^2	0.977	n.d.	n.d.
	Correlation	0.910	n.d.	n.d.

by the correlation factors and the R^2 reported in Table 2. Considering that the experimental behavior onto all materials is always satisfactorily represented by the Freundlich isotherm, this model was adopted for comparison purposes, as reported in Fig. 4(a).

The behavior of the tested materials could be better evaluated by dividing the whole investigated experimental range of toluene equilibrium dissolved concentrations into three intervals—namely, from 0 to 50, 50 to 250 and over 250 mg L^{-1}. At the lower concentration level, AC and SWCNTs behave similarly, with an adsorption capacity significantly higher than that of MWCNTs (which in this range shows negligible toluene removal). In the intermediate concentration range (50–250 mg L^{-1}), AC does not have a significantly increased toluene sorbed amount with increasing dissolved toluene concentration, whereas SWCNTs quasi-linearly increase the toluene removal by a factor of 4 with respect to AC. In this range, MWCNTs start to significantly increase their adsorption ability, and at the highest concentration, the removal is similar to AC. Above 250 mg L^{-1}, the MWCNTs start to exhibit significant toluene removal with respect to AC, whereas SWCNTs still behave better than AC and MWCNTs.

Das et al. [33] illustrated that the significantly higher toluene affinity for SWCNT surfaces, with respect to MWCNTs, could be explained by their lower diameter; this aids the adsorption phenomena by a strong interaction between CNT diameter and adsorbate size. Moreover, adsorption onto CNTs has been strongly associated with their high surface area [34,35]. Thus, toluene adsorption has been normalized for the material surface area. Fig. 4(b) reports the adsorption experimental data in terms of milligrams of toluene per square meter of sorbent as a function of toluene equilibrium dissolved concentration. The normalized adsorption, q_e (mg m^{-2}), was calculated by using the surface areas reported in the Sigma-Aldrich® and CheapTubes® technical sheets, respectively, for AC and CNTs. The good superimposition of the two CNT experimental isotherms allowed the specific surface area to be identified as responsible for

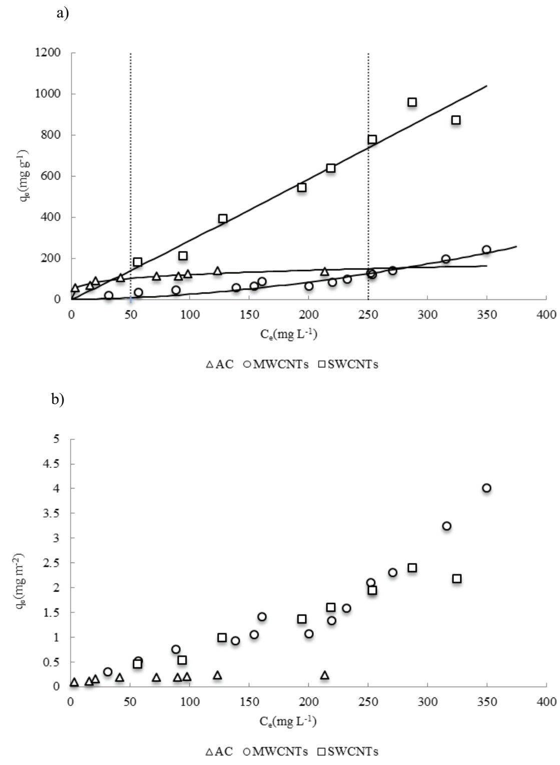

Fig. 4. Comparison of the experimental and calculated adsorption isotherms onto activated carbon, multi-walled carbon nanotubes and single-walled carbon nanotubes (equilibrium tests) in deionized water: (a) toluene sorbed amount in terms of mg g^{-1} and (b) toluene sorbed amount in terms of mg m^{-2}.

the adsorption of toluene onto nanotubes independently of their diameter. Moreover, the significantly higher adsorption capacity of CNTs with respect to AC is confirmed. As already reported by Das et al. [35], this behavior can be explained assuming that the available π electrons on graphene sheets stimulate the formation of a strong complex between the CNT surface and the aromatic dissolved contaminant. The same conclusions were also drawn by Yu et al. [24] who considered π-π interactions the base of the strong adsorption of toluene onto CNTs surface.

Considering the adsorption tests carried out in synthetic seawater, AC, MWCNT and SWCNT data were fitted with the same models already used in deionized water. AC fitting was carried out with the Langmuir and Freundlich models, whereas that of MWCNTs and SWCNTs was conducted with the linear and Freundlich models according to the observed experimental behavior. Table 2 reports the optimized values, the R^2 and the correlation factors for the AC, MWCNT and SWCNT adsorption tests with the selected models. Also, in this case, the Freundlich isotherm was adopted for the comparison of the three sorbent materials. Adsorption tests performed in synthetic seawater, as reported in Fig. 5(a), confirmed the relative behavior among the different sorbents already observed in the deionized water. It must be noticed that in this case, MWCNT adsorption overtakes AC adsorption at a slightly lower concentration with respect to deionized water. As shown in Fig. 5(b), where the toluene adsorption is reported in terms of mg m^{-2}, the CNT surface area seems to drive their adsorption capacity. In addition, in synthetic seawater, the significantly higher toluene adsorption onto CNTs with respect to AC has been confirmed.

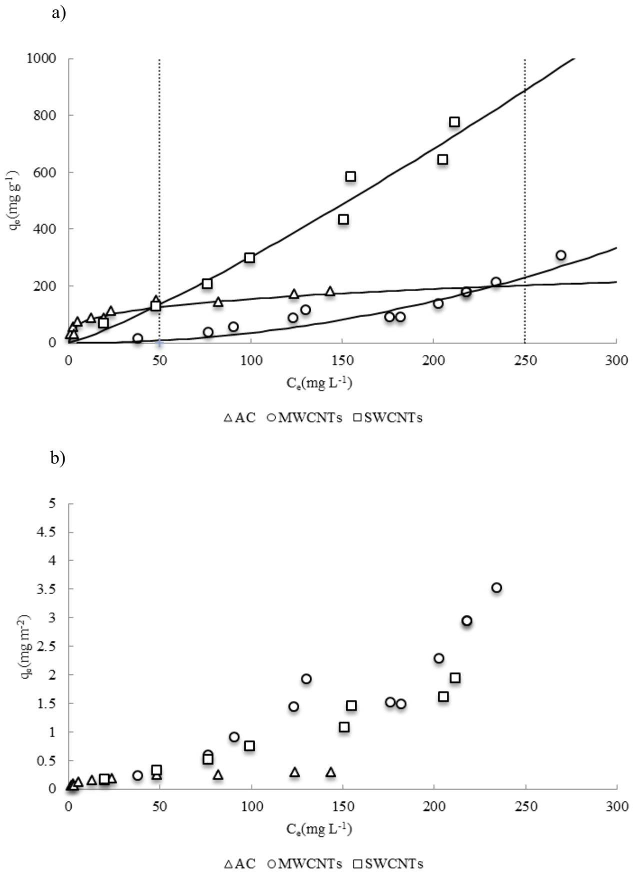

Fig. 5. Comparison of the experimental and calculated adsorption isotherms onto activated carbon, multi-walled carbon nanotubes and single-walled carbon nanotubes (equilibrium tests) in seawater: (a) toluene sorbed amount in terms of mg g^{-1} and (b) toluene sorbed amount in terms of mg m^{-2}.

In general, the adsorption of toluene onto all tested materials always appears greater in synthetic seawater than in deionized water, confirming the hydrophobicity characteristic of the adsorption mechanism. Indeed, the salinity causes the material surface to be more attractive for toluene in sea salt solution. Moreover, the sea salt solution enhances the hydrophobic characteristic of the toluene, increasing its adsorption onto the sorbent surface.

4. Conclusions

A deep characterization of two different types of CNTs was experimentally carried out to investigate their possible use for environmental applications, such as sorbent to be used in booms or as sediment amendments for oil spill remediation. CNT performance was also compared with the more conventional sorbent, AC.

Kinetic batch tests, carried out in both deionized and synthetic seawater, have clearly shown a faster adsorption of the dissolved toluene onto CNTs with respect to AC.

The salinity has a more positive effect on the kinetics of CNTs, and this could be very advantageous in their prospective use for marine oil spill remediation (booms). Moreover, the high removal capacity of the CNTs observed in the highest concentration level of the hydrophobic contaminants could be especially relevant for the possible use of these materials for environmental applications, in which the contaminant concentration could be particularly high.

At the present time, the major drawbacks in the use of CNTs are associated with the high production costs and the uncertain toxic effect due to their large mobility. The SWCNTs and the MWCNTs cost is on average much higher of the AC one: 90, 12, 1×10^{-3} \$ per gram of material, respectively [36]. Furthermore, the lack of consolidated industrial processes for CNT synthesis may restrict large-scale nanotube applications, especially for single-walled nanotubes, although Piccinno et al. [37] have reported a clear increase in CNT production in recent years. On the other hand, the use of CNTs can be legitimated if the regeneration is taken into account. By this regard, Lu et al. (2008) [36] observed that CNTs maintain their sorption capacity after several regeneration cycles whereas AC strongly lowers its adsorption capacity.

AC is a consolidated material largely used for environmental applications, whereas CNT use is still connected to lab-scale applications. Despite these problems, the high CNT adsorption performance, the possibility to easily functionalize the material's surface, thus extending its potential applicability to a large class of contaminants, and the regeneration efficiency makes them potentially suitable materials for environmental application. Consequently, the potential increase in the market request for these materials should positively affect the cost of CNTs, establishing them within the next years as a feasible alternative with respect to the more consolidated sorbent amendments. The potential toxic effect could then be effectively controlled and reduced by incorporating the CNTs in porous polymer matrices specifically designed for in situ treatment.

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