



Adsorption of linear alkylbenzene sulfonates on carboxyl modified multi-walled carbon nanotubes



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HIGHLIGHTS

- LAS adsorption on CMMWCNTs can be well described using the Freundlich equation.
- Hydrophobic and hydrogen bond interactions strongly affect LAS adsorption.
- Highest LAS adsorption occurs at certain ionic strengths depending on the cations.

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ABSTRACT

Understanding of the adsorption behavior of organic pollutants on carbon nanotubes (CNTs) and its governing factors are crucial for the assessment of transport and fate of organic pollutants. This study explored adsorption characteristics of linear alkylbenzene sulfonates (LAS) on carboxyl modified multi-walled carbon nanotubes (CMMWCNTs) and the effect of solution chemistry and temperature on LAS sorption. Results indicated LAS adsorption isotherms to display five distinct regions of sorption at 25 °C and 60 °C. Regardless of temperature, the adsorption isotherm of LAS on the CMMWCNTs was well described using the Freundlich equation. This result indicated heterogeneous distribution of adsorption sites on the CMMWCNT surface. At low initial LAS concentrations, below the critical micelle concentration, (2, 10 and 50 mg L⁻¹) LAS adsorption on the CMMWCNTs followed pseudo second-order kinetics. The highest LAS adsorption was observed at ionic strengths of 1.0 mol L⁻¹ for NaCl; and 0.2 mol L⁻¹ for both CaCl₂ and MgCl₂. However, LAS sorption was greatest in the presence of sodium-divalent anion salts and at higher temperatures. These findings are of relevance to the fate and environmental risk of LAS in the presence of CMMWCNTs in high salinity wastewaters or effluents and brackish receiving surface water bodies (e.g., at estuaries).

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1. Introduction

Due to their unique and outstanding structural, electronic, mechanical, and chemical and physical properties [1,2], carbon nanotubes (CNTs) have been extensively investigated as biomaterials, multi-functional composites and electronic components [3–5].

On account of their highly porous and hollow structure, large specific surface area, low density and strong interaction with various chemicals, CNTs have received wide attention as adsorbents for the removal of inorganic and organic contaminants from water and gases [6–11]. Modified CNTs have been shown to be fast and efficient for the adsorption of organic contaminants and heavy metals from aqueous solution [12,13]. For example, the oxidation of carbon nanotubes by NaClO, HNO₃, H₂O₂ or KMnO₄ introduces oxygen containing functional groups (e.g., –COOH, –OH, or =CO) onto the surface of the tubes thereby changing the wettability of CNT surfaces, making the tubes more hydrophilic and better able

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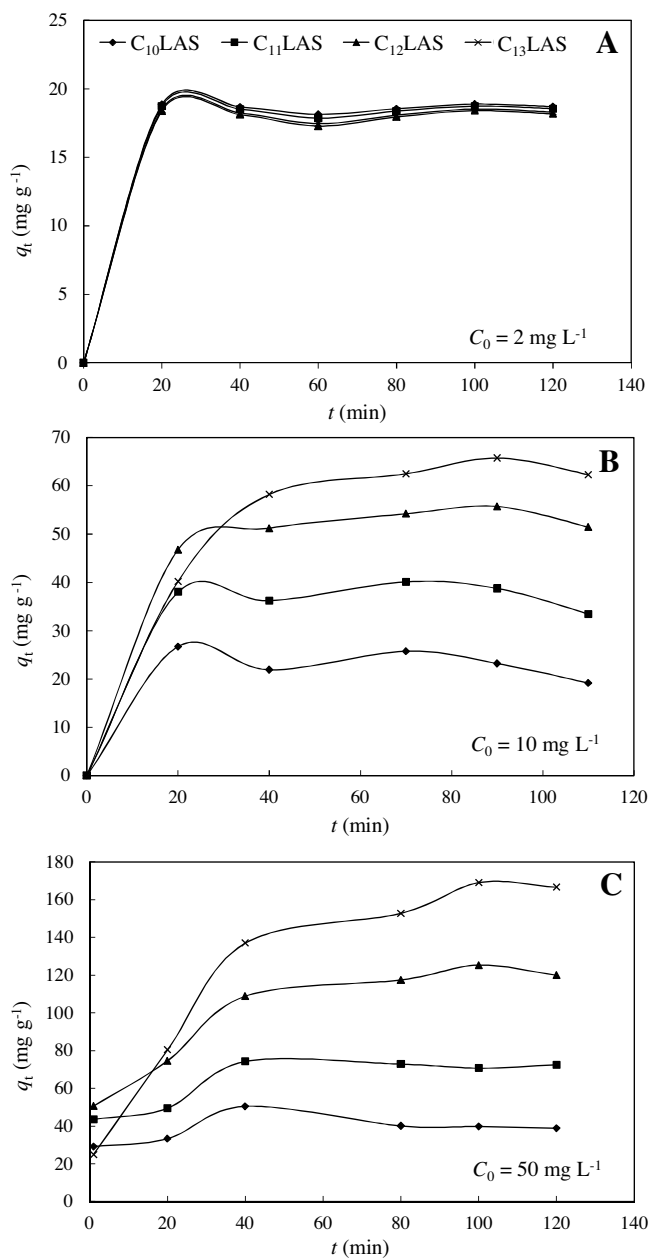


Fig. 1. Adsorption kinetics of LAS at different initial concentrations on the CMMWCNTs (initial total LAS concentration: (A) 2 mg L⁻¹, (B) 10 mg L⁻¹, and (C) 50 mg L⁻¹; 10 mL; 0.01% (w/v) CMMWCNTs; pH 5.0; agitation speed 200 rpm; 25 °C; 0.1 mol L⁻¹ NaCl).

to be dispersed in aqueous solution and increasing their adsorption capacities of contaminants [14–17].

On account of their wide application, CNTs have been intentionally and accidentally released into the environment during production, use and disposal. This has raised serious concerns regarding their potential environmental impacts [17,18]. A significant concern is that once released to aquatic environments, carbon nanotubes might interact with contaminants present in water bodies and significantly affect the fate of contaminants following their association with CNTs [7]. The effects of the interactions between contaminants and CNTs, which are often functionalized and exhibit enhanced stability and mobility in the aqueous environment [5], on the behavior of CNTs in varying natural environments is still poorly understood. In particular, the understanding of the adsorption behavior of organic pollutants on CNTs and identification of

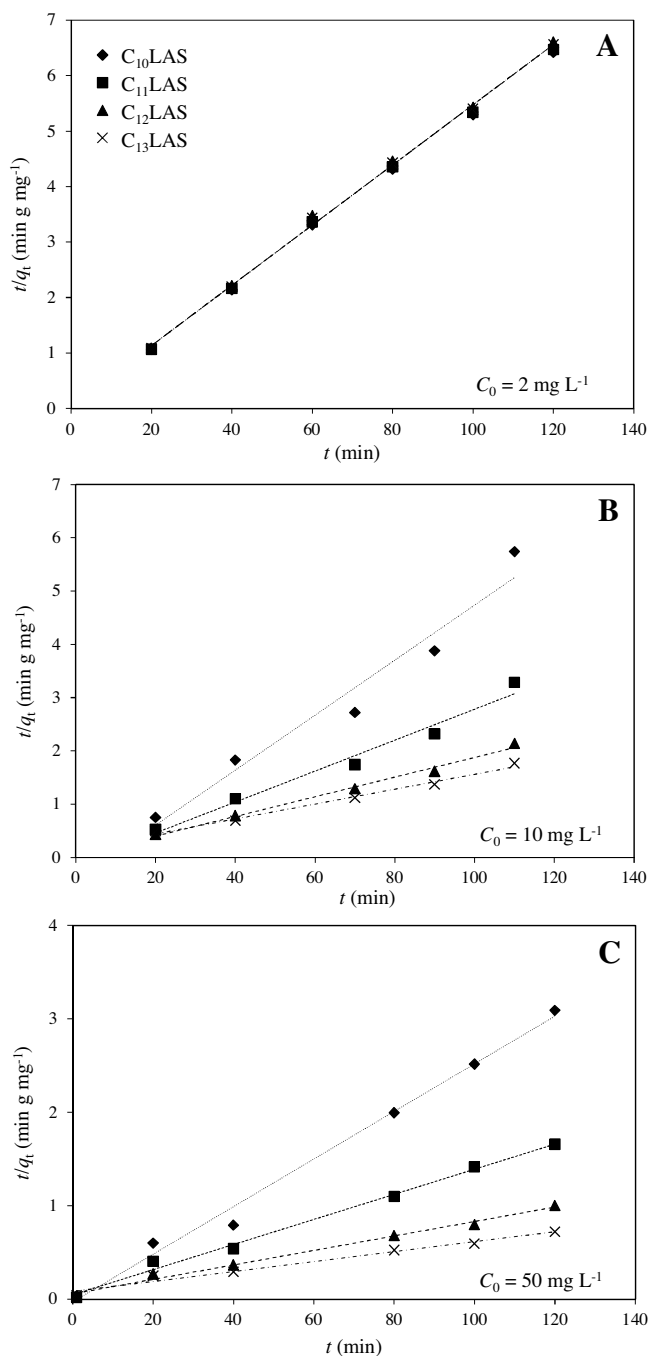


Fig. 2. Fitted adsorption kinetics data of LAS at different initial concentrations on the CMMWCNTs using pseudo second-order kinetics model (initial total LAS concentration: (A) 2 mg L⁻¹, (B) 10 mg L⁻¹, and (C) 50 mg L⁻¹; 10 mL; 0.01% (w/v) CMMWCNTs; pH 5.0; agitation speed 200 rpm; 25 °C; 0.1 mol L⁻¹ NaCl).

its principal influencing factors are critically important for predicting the fate and environmental risk of organic pollutants in aquatic environments.

Linear alkylbenzene sulfonates (LAS), are commercial anionic surfactants often found as a pollutant in surface waters [19]. LAS constitutes at least 20% of the worldwide surfactant production [19]. Over 40 years, LAS has been widely used in household cleaning detergents, personal care products and industries such as textiles, paints, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery and pulp and paper [20]. As a result, considerable amounts of LAS have been released into surface waters through wastewaters and sewage effluents. The release of LAS poses a threat

of adverse impacts on water quality and aquatic habitats [21,22]. It has been reported that the adsorption of surfactants on CNTs could lead to the modification of the CNTs surfaces and thus affect the CNTs' efficiency in removing metal ions (e.g., nickel) [23] and organic contaminants (e.g., naphthalene, oxytetracycline) [24,25] from water. The association of surfactants and CNTs could occur resulting from the mixing in influent streams before treatment, post-discharge mixing in surface waters and intentional or accidental release into the environment. Addition of surfactants to CNTs-containing wastewater to improve the dispersibility and the stability of the CNTs could enhance the stabilization of CNTs in water via π - π stacking [26,27]. Increasing the number of phenyl rings contained in the surfactant tails, from one to three, has been reported to lead to stronger π - π interactions between surfactant tails and MWCNT surfaces [28]. Therefore, the surfactant-coated CNTs exhibit higher mobility than uncoated CNTs, possibly causing greater ecological effect and even deep migration into groundwater [29].

Our previous study showed that the removal efficiency of linear alkylbenzene sulfonates (LAS) by a carboxyl modified multi-wall carbon nanotubes (CMMWCNTs) column (for solid phase extraction) from the spiked environmental water samples was >80% [30]. Therefore, recognizing the influencing factors on LAS adsorption by CNTs is important for predicting their fates and elucidating possible complex effects of their co-existence and interactions on the aquatic environment. However, to our knowledge, the bulk of the research work involving both CNTs and surfactants has been related to the dispersion and stabilization of CNTs [26,27,31], few studies have systematically investigated the influence of environmental parameters of the aqueous phase on the adsorption of LAS on CNTs, particularly in high salinity or warm water conditions.

The objectives of this study were to reveal the adsorption characteristics (kinetics and isotherm) of a mixture of four LAS homologues on CMMWCNTs and to investigate the effects of water chemistry parameters and temperature. These factors are of relevance to likely discharge scenarios wherein salinity and temperature could be elevated. Such scenarios include: high salinity conditions are often observed in industrial wastewaters and brackish surface waters. Salt concentrations in the range of 500–30,000 mg L⁻¹ commonly occurred as a result of civil engineering projects such as dikes and flooded coastal marshland used for freshwater prawn farming or at estuaries where fresh water meets seawater. The salinity of brackish surface waters can vary considerably over space and time [32]. A wide range of elevated temperature can be found in the influent streams of wastewater treatment plant, which receive wastewaters from processes such as cleaning and disinfecting at 60 °C and knife sterilization at 82 °C [33].

2. Materials and methods

2.1. Materials

CMMWCNTs with outer diameters of 20–30 nm, a length of about 30 μ m, carboxyl (-COOH) content of 1.23%, hydroxyl (-OH) content of 1.76%, minor content of carbonyl (-C=O) and a surface area of above 110 m² g⁻¹, were purchased from R&D Center of Carbon Nanotubes, Chengdu Organic Chemicals Co., Chinese Academy of Sciences. Commercial LAS mixture (C₁₀LAS (CH₃(CH₂)₉C₆H₄SO₃Na; 19.16%), C₁₁LAS (CH₃(CH₂)₁₀C₆H₄SO₃Na; 30.1%), C₁₂LAS (CH₃(CH₂)₁₁C₆H₄SO₃Na; 28.65%) and C₁₃LAS (CH₃(CH₂)₁₂C₆H₄SO₃Na; 22.09%)) was supplied by Sigma-Aldrich. HPLC grade methanol and acetonitrile were purchased from Scharlau Chemie S. A., Spain. Sodium chloride, calcium chloride magnesium chloride, acetone, hydrochloric acid, sodium hydrox-

ide and all other chemicals used were of analytical reagent grade (Tianjin Bodie Chemical Co., Ltd., China).

2.2. Instrumental analysis

The analysis of water sample for LAS was performed by using a HPLC equipped with a UV detector (JASCO, Tokyo, Japan) at 275 nm. Injection was carried out by using a Rheodyne valve (Rohnert Park, CA) with a sample loop volume of 20 μ L. Chromatographic separation was performed on a Symmetry C8 column (150 mm \times 4.6 mm, 5 μ m) (Waters Cooperation, USA) with security guard column. The mobile phase used in the chromatographic separation consisted of a binary mixture of methanol and water (containing 0.5 mmol L⁻¹ sodium acetate) with the ratio of 78:22 at a flow rate of 0.5 mL min⁻¹. The column temperature was 30 °C.

2.3. Adsorption experiments

2.3.1. Adsorption kinetics

Adsorption kinetics of LAS on the CMMWCNTs were assessed using a batch equilibrium method at 25 °C. Solutions with different initial total LAS concentrations (2, 10 and 50 mg L⁻¹) in deionized water containing 0.1 mol L⁻¹ NaCl as electrolyte were added to 100 mL glass jars with Teflon screw caps containing 0.01% (w/v) CMMWCNTs, the pH was adjusted using dilute HCl solution or NaOH solution to pH 5.0 (our preliminary results showed pH 5.0 was the optimum pH value to obtain a maximum adsorption). During the experiments, samples were agitated in a shaking water bath, held at the desired temperature, at a constant speed of 200 rpm. Samples were taken at time interval of 20 or 30 min and centrifuged at 3000 rpm for 30 min and supernatants filtered through 0.45 μ m filter. The final concentrations of LAS remaining in the aqueous phase were determined using HPLC-UV after SPE enrichment. The duration of each kinetic experiment was at least 120 min.

The amounts of LAS adsorbed and adsorption efficiencies for the CMMWCNTs were calculated by applying Eqs. (1) and (2), respectively:

$$q_e = V(C_0 - C_e) / W \quad (1)$$

$$X = (C_0 - C_t) / C_0 \times 100\% \quad (2)$$

where q_e is the amount of LAS adsorbed by the adsorbent CMMWCNTs at equilibrium (mg g⁻¹), C_0 is the initial LAS concentration in the aqueous phase (mg L⁻¹), C_t is the LAS concentration in the aqueous phase at a given time t (h) (mg L⁻¹), C_e is the LAS equilibrium concentration in the aqueous phase after the batch adsorption procedure (mg L⁻¹), W is the mass of the adsorbent CMMWCNTs (g) and V is the volume of LAS solution (L), X is the percentage of LAS adsorbed on CMMWCNTs at a given time t .

A pseudo second-order equation (Eq. (3)) was used to gain insight into the kinetics:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t = \frac{1}{v_0} + \frac{t}{q_e} \quad (3)$$

where q_t (mg g⁻¹) is the amount of LAS adsorbed on the CMMWCNTs at a given time t (h), k_2 (g mg⁻¹ min⁻¹) is the adsorption rate constant of the pseudo second-order model and v_0 is the initial adsorption rate (mg min⁻¹ g⁻¹).

2.3.2. Adsorption isotherms

Adsorption isotherms of LAS on the CMMWCNTs were obtained using a batch equilibrium method in 10 mL glass vials with Teflon screw caps containing 0.05% (w/v) CMMWCNTs at 200 rpm shaker, held at the desired temperature, for 300 min. Preliminary kinetics experiments indicated that 300 min was sufficient time for equilibrium to be achieved, across a wide range of initial total LAS

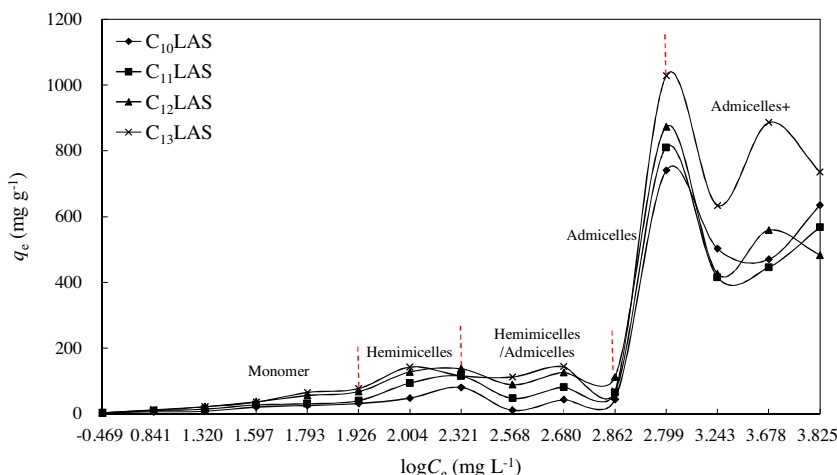


Fig. 3. Five-region adsorption isotherm of LAS on the CMMWCNTs at 25 °C (initial total LAS concentration 0–7000 mg L⁻¹; 10 mL; 0.05% (w/v) CMMWCNTs; pH 5.0; agitation speed 200 rpm; 0.1 mol L⁻¹ NaCl).

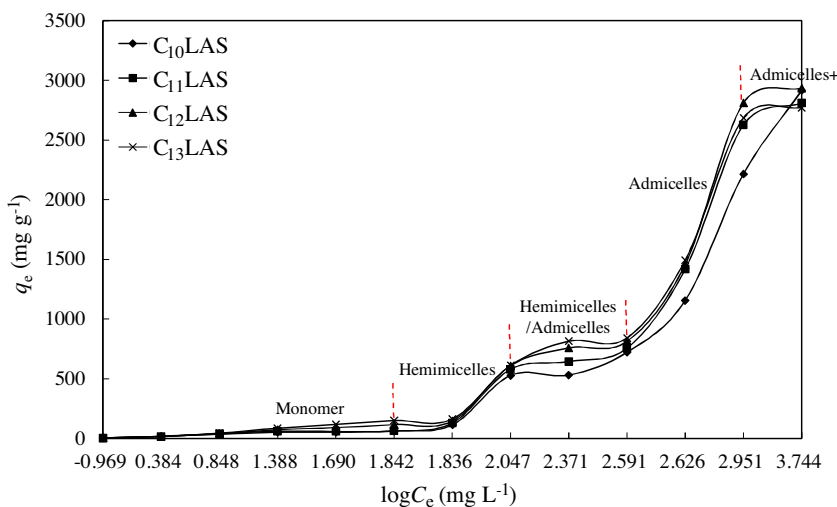


Fig. 4. Five-region adsorption isotherms of LAS on the CMMWCNTs at 60 °C (initial total LAS concentration 0–7000 mg L⁻¹; 10 mL; 0.05% (w/v) CMMWCNTs; pH 5.0; agitation speed 200 rpm; 0.1 mol L⁻¹ NaCl).

concentrations (up to 7000 mg L⁻¹; data not shown). The adsorption experiments were performed at 25 °C and 60 °C and the LAS solutions were prepared at different total concentrations ranging from 0 to 7000 mg L⁻¹ at constant pH 5.0 in 0.1 mol L⁻¹ NaCl. After equilibration, the samples were treated the same way as for the kinetics experiments.

Langmuir equation (Eq. (4)) and Freundlich equation (Eq. (5)) were used to fit the adsorption data of LAS on the CMMWCNTs

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

where q_e is the amount of LAS adsorbed per unit mass of CMMWCNTs at equilibrium (mg g⁻¹), C_e is equilibrium concentration of LAS in the aqueous phase (mg L⁻¹), q_m is the maximum adsorption capacity (mg g⁻¹), K_L (L mg⁻¹) is the adsorption equilibrium constant of Langmuir model related to the affinity of binding sites, K_F (L mg⁻¹) is Freundlich coefficient related to adsorption capacity and n is a dimensionless parameter related to adsorption intensity of the adsorbent.

Since satisfactory repeatability (relative standard deviations on q_t and q_e were all <4.8%) of replicate measurements had been achieved in the preliminary testing, the adsorption kinetics and isotherm experiments were conducted without replicates to minimize the number of experimental sets.

2.3.3. Effects of aqueous solution composition and temperature

The effect of solution composition was explored using different concentrations of NaCl, CaCl₂ and MgCl₂ ranging from 0 to 1.0 mol L⁻¹. NaCl, NaF, NaNO₃ and Na₂SO₄ were added individually into the LAS solutions at the same anion concentration (0.8 mol L⁻¹) of Cl⁻, F⁻, NO₃⁻ and SO₄²⁻ to determine the effect of co-existing anions on LAS adsorption on the CMMWCNTs ($n = 3$). The effect of temperature was investigated at 25, 40, 50 and 60 °C. For this part of study, the LAS solutions used were prepared at the same initial total concentration of 200 mg L⁻¹ (concentration is in the range of the LAS level found in wastewater [21,34]) at constant pH 5.0. All the adsorption condition and treatment were consistent with those for the adsorption isotherm experiment.

This part of study, which investigated the effect of influencing factors, was conducted in triplicate and the working solutions of desired concentrations were prepared daily.

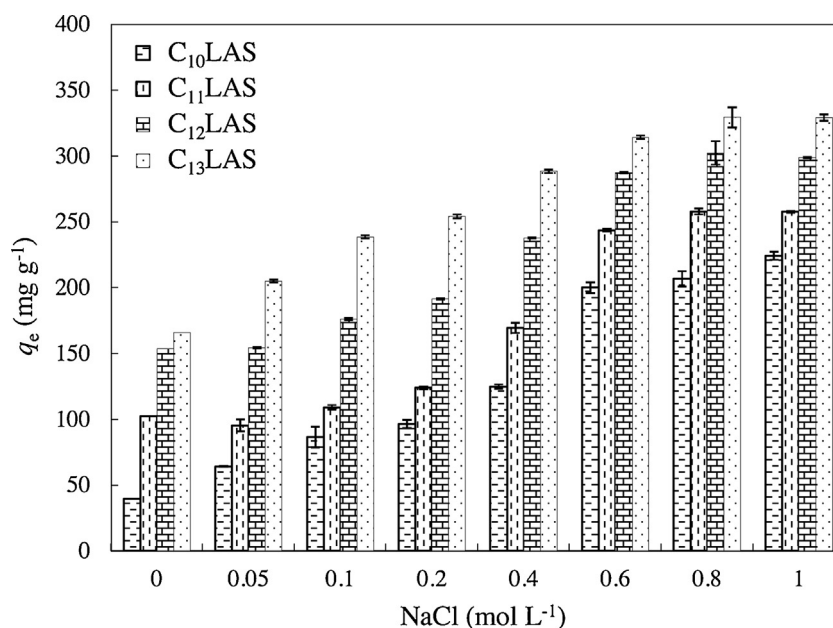


Fig. 5. Effect of NaCl concentration on LAS adsorption on the CMMWCNTs (initial total LAS concentration 200 mg L^{-1} ; 10 mL ; 0.05% (w/v) CMMWCNTs; pH 5.0; equilibration time 300 min ; agitation speed 200 rpm ; 25°C ; results were average \pm standard deviation of three replicates).

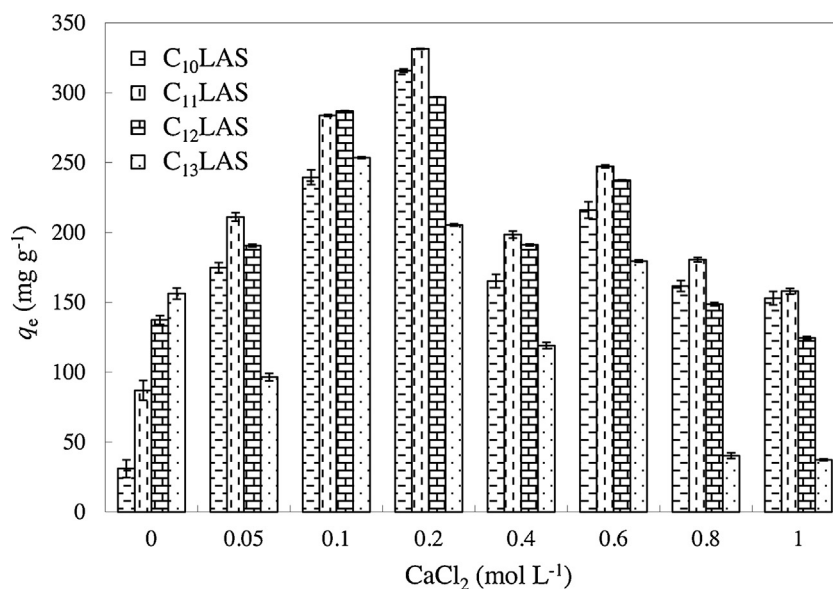


Fig. 6. Effect of CaCl_2 concentration on LAS adsorption to the CMMWCNTs (initial total LAS concentration 200 mg L^{-1} ; 10 mL ; 0.05% (w/v) CMMWCNTs; pH 5.0; equilibration time 300 min ; agitation speed 200 rpm ; 25°C ; results were average \pm standard deviation of three replicates).

3. Results and discussion

3.1. Adsorption kinetics

3.1.1. Effects of initial LAS concentration

Kinetics of LAS adsorption on the CMMWCNTs is presented in Fig. 1. Depending on alkyl chain length of LAS, adsorption dramatically increased in the first 20 or 40 min and reached equilibrium within 100 min. Where initial LAS concentrations were lower, less time was required to reach equilibrium. For the lowest initial total LAS concentration of 2 mg L^{-1} , the adsorption equilibrium of all four LAS homologues was reached within 20 min and showed no significant changes from 20 to 120 min (Fig. 1(a)). For the medium initial total LAS concentration of 10 mg L^{-1} , only C_{10}LAS and C_{11}LAS adsorption reached equilibrium within 20 min while adsorption of

C_{12}LAS and C_{13}LAS needed a longer time (100 min) to reach equilibrium (Fig. 1(b)). For the highest initial total LAS concentration (50 mg L^{-1}), it took more time (40 min) for the adsorption of short alkyl chain C_{10} and C_{11}LAS homologues to reach equilibrium (q_e : 39.3 and 71.6 mg g^{-1} , respectively) while the adsorption equilibrium of C_{12}LAS and C_{13}LAS (q_e : 123 and 168 mg g^{-1} , respectively) was achieved within 100 min (Fig. 1(c)). The adsorbed amount of LAS on the CMMWCNTs at equilibrium (q_e) was higher for LAS with longer alkyl chain at high initial total LAS concentration (i.e., 10 and 50 mg L^{-1}). The observed early rapid adsorption was probably due to the initially abundant number of active sites on the CMMWCNTs, and with the gradually increased occupancy of these sites, the sorption process became less efficient with increasing time. Such a mechanism was proposed by Heibati et al. [35] and Neibi et al. [36]. Adsorption efficiency (X) of individual LAS homologues at differ-

Table 1
Adsorption efficiency (X) of individual LAS homologues on the CMMWCNTs at different times during the kinetics experiment (0.01% (w/v) CMMWCNTs; pH 5.0; 25 °C; 0.1 mol L⁻¹ NaCl).

Initial total LAS concentration (mg L ⁻¹)	Time (min)	X of C ₁₀ LAS (%)	X of C ₁₁ LAS (%)	X of C ₁₂ LAS (%)	X of C ₁₃ LAS (%)
2	20	94.3	93.7	92.0	92.4
	40	93.4	92.6	90.6	91.2
	60	90.7	89.3	86.4	87.3
	80	92.7	91.9	89.7	90.4
	100	94.4	93.7	92.1	92.6
	120	93.5	92.7	90.9	91.5
	180	95.2	94.6	93.4	93.8
10	20	26.7	38.0	46.88	40.2
	40	21.9	36.2	51.2	58.2
	70	25.8	40.1	54.2	62.5
	90	23.2	38.8	55.7	65.8
	110	19.2	33.5	51.4	62.3
	130	24.5	40.5	58.2	69.6
	150	28.5	45.3	62.3	74.4
	170	31.9	48.7	64.8	75.7
50	1	5.8	8.7	10.1	5.0
	20	6.7	9.9	14.9	16.1
	40	10.1	14.9	21.8	27.4
	60	6.6	10.9	17.8	22.7
	80	8.0	14.6	23.5	30.6
	100	8.0	14.1	25.1	33.8
	120	7.8	14.5	24.0	33.3

ent time points during the kinetics experiment are summarized in Table 1. For the low initial concentration of 2 mg L⁻¹, the adsorption efficiencies of C₁₀LAS, C₁₁LAS, C₁₂LAS and C₁₃LAS after reaching equilibrium were above 90.7%, 89.3%, 86.4% and 87.3%, respectively, but much lower adsorption efficiencies at equilibrium were observed (around 7.77%, 14.5%, 24.0% and 33.3%, respectively) for the higher initial concentration of 50 mg L⁻¹. Adsorption efficiency decreased with increasing initial total LAS concentration. This outcome is in keeping with the sorption site filling conceptualization described above.

Various mechanisms such as π - π electron-donor-acceptor interaction, hydrogen bonding, electrostatic interaction and hydrophobic interaction have been proposed, which simultaneously act on the adsorption of organic chemicals on CNTs [37–39]. Triton X and the hydroxyl/carboxylic groups on CNTs surface was reported to form hydrogen bonds [39,40].

The adsorbed amount of LAS was also considered on a molar basis (i.e. with unit $\mu\text{mol g}^{-1}$ and is referred to as q_e'). While an unconventional unit to express q_e' a molar consideration allows better appreciation of LAS-CMMWCNT interaction on a molecular (rather than mass) basis. In this analysis the relative changes in q_e' across homologue groups were different to those were mass units were used. The overall trend (as reported above) did not change when molar units were used. For example, at initial total LAS concentration of 10 mg L⁻¹, q_e' were 76.4, 112, 154 and 177 $\mu\text{mol g}^{-1}$ for C₁₀LAS, C₁₁LAS, C₁₂LAS and C₁₃LAS, respectively; and at 50 mg L⁻¹ initial total LAS concentration, q_e' were much higher all the four LAS homologues with longer alkyl chain (123, 215, 352 and 463 $\mu\text{mol g}^{-1}$ for C₁₁LAS, C₁₂LAS and C₁₃ LAS, respectively).

Thus, the overarching outcome was one where the adsorption ability (q_e and q_e') of CMMWCNTs was stronger for LAS with longer alkyl chain at relatively high initial total LAS concentrations (10 and 50 mg L⁻¹) while no significant differences between LAS with different alkyl chain lengths were found at low initial total LAS concentration (2 mg L⁻¹). This overarching outcome reflects greater opportunity for hydrogen bond interaction between larger LAS molecules with longer alkyl chain and CMMWCNTs. Increasing alkyl chain length may lead to the decrease of the critical micelle concentration (CCC; the minimum concentration of ions needed to cause rapid coagulation of colloids) and increase of the hydropho-

bicity of the surfactant molecule [41], and with the addition of successive methyl groups to the alkyl chain of LAS the adsorption free energy were increased [42]. Therefore, we speculate that longer alkyl chain LAS can be more easily adsorbed by CMMWCNTs owing to their higher hydrophobicity. On the other hand, the adsorption of LAS could better disperse the CMMWCNTs aggregates at higher concentration of LAS in solution, which may facilitate the adsorption of LAS by exposing more adsorption sites.

3.1.2. Modelling of adsorption kinetics

The adsorption process of LAS, at all tested initial concentrations, on the CMMWCNTs could be well represented by the pseudo second-order model (Fig. 2). The correlation coefficients (R^2) for the pseudo second-order fitting fell in the range 0.958–0.999. The good of fitness with the pseudo second-order model indicated that the adsorption rate was controlled by chemical adsorption and the adsorption capacity correlated to the numbers of active sites on CMMWCNTs to receive LAS molecules [43,44]. The values of pseudo second-order rate constants k_2 (Table 2) suggest that adsorption sites on the CMMWCNTs were more readily available at lower initial LAS concentrations and for LAS homologue with shorter alkyl chains.

3.2. Adsorption isotherm

3.2.1. Characteristics of adsorption isotherms at two temperatures

The adsorption isotherms studies were carried out at two different temperatures (25 and 60 °C) (Figs. 3 and 4). As the temperature increased from 25 to 60 °C, the adsorption amount (q_e) of CMMWCNTs at equilibrium for C₁₀-C₁₃LAS increased from: 740 to 2214 (C₁₀LAS); 810 to 2624 (C₁₁LAS); 873–2809 (C₁₂LAS); 1027 to 2683 mg g⁻¹ (C₁₃LAS).

It has been proposed, with the increasing of surfactant concentration, that surfactant molecules adsorb initially as monomers, then as hemimicelles, then as mixed hemimicelles and admicelles, then as admicelles, and finally, as mixed admicelles [45]. In the present study, the LAS adsorption isotherm exhibited a continuous transition from monolayer to bilayer aggregation. Three and five region adsorption isotherm have been reported for surfactants on metal oxide [45], indicating the dominant contribution

Table 2

Estimated parameters by fitting pseudo second-order kinetics model to the measured sorption kinetics data of LAS on the CMMWCNTs (0.01% (w/v) CMMWCNTs; pH 5.0; 25 °C; 0.1 mol L⁻¹ NaCl).

Initial total LAS concentration (mg L ⁻¹)		$k_2 \times 10^{-2}$ (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	q_e^* (mg g ⁻¹)	R ²
2	C ₁₀ LAS	3.375	18.8	18.8	0.999
	C ₁₁ LAS	2.889	18.7	18.6	0.999
	C ₁₂ LAS	2.158	18.3	18.3	0.998
	C ₁₃ LAS	2.272	18.4	18.4	0.999
10	C ₁₀ LAS	0.175	19.4	23.2	0.958
	C ₁₁ LAS	0.125	34.5	38.8	0.976
	C ₁₂ LAS	0.099	54.4	55.7	0.993
	C ₁₃ LAS	0.052	71.4	65.8	0.989
50	C ₁₀ LAS	2.226	39.2	39.3	0.992
	C ₁₁ LAS	0.374	74.6	71.6	0.994
	C ₁₂ LAS	0.105	130	123	0.990
	C ₁₃ LAS	0.034	189	168	0.979

q_e : value obtained by model fitting; q_e^* : measured value.

of dispersive forces in promoting self-association and a continuous transition from monolayer to bilayer aggregation.

The adsorption isotherms (q_e against $\log C_e$) of LAS at 25 °C (Fig. 3) and 60 °C (Fig. 4) showed five-region mode of adsorption. For the 25 °C-adsorption isotherm of LAS: in the first region, the adsorption isotherm increased gently with increasing LAS concentration in range of 2–125 mg L⁻¹, indicating LAS molecular adsorbed sparsely as monomers via hydrophobic interaction and hydrogen bonding [46] on CMMWCNTs surfaces. In the second region, both the hydrophobic interactions between LAS molecules and the dispersion of the CMMWCNTs promoted surfactant assembly, leading to a moderate increase of q_e as the hemimicelles structures formed. In the third region, with the increased number of LAS molecules adsorbed on CMMWCNTs, the electrostatic repulsion force between LAS molecules (admicelles) induces a decrease of adsorption (as hemimicelles). In the fourth region, dispersive forces among dissolved LAS monomers and surface mono-layered aggregates promoted surfactant adsorption and the formation of bilayered structures (admicelles) [45], leading to substantial increase of adsorption ability (q_e). In the fifth region, the adsorption reached a plateau because the electrostatic repulsion forces between LAS molecules progressively hindering further surfactant adsorption. The third region of the 60 °C-adsorption isotherm of LAS (Fig. 4) was different from that of the adsorption isotherm at 25 °C (Fig. 3). The 25 °C-adsorption isotherm decreased with increasing $\log C_e$ at the third region while the 60 °C-adsorption isotherm showed a moderate increase. This phenomenon may have two reasons: firstly, the electrostatic repulsion force between LAS molecules was greater at lower temperature, which hindered the formation of the adsorbed LAS bilayer on the surface of CMMWCNTs; secondly, higher temperature can cause the decrease of the hydration of the surfactants' hydrophilic groups and the resulting increase of micellization [47], and the formed admicelles and hemimicelles are then adsorbed by CMMWCNTs surface at LAS concentrations above the critical micelle concentration.

3.2.2. Modelling adsorption isotherm

The obtained adsorption isotherms represent the distribution of LAS molecules between the solid and aqueous phase when the adsorption reached equilibrium. The Langmuir isotherm [48,49] assumes that the adsorbent surface is homogeneous; it is mainly suitable for monolayer adsorption on smooth and homogeneous surface, and; a site can only be occupied by one pollutant molecule [44]. The Freundlich model is mainly suitable for adsorption on surfaces with no uniform energy distribution which means the adsorption is heterogeneous [50,51].

The Langmuir and Freundlich parameters and calculated coefficients are shown in Table 3. It is clear that the experimental data at both 25 °C and 60 °C was generally better represented by the Freundlich isotherm than by the Langmuir isotherm. This indicates, that regardless of the temperature, the process of LAS adsorption onto the CMMWCNTs occurred on a largely heterogeneous CMMWCNT surface. The value of Freundlich parameter $1/n < 1$ indicates that LAS homologues of different carbon chain lengths were all readily adsorbed on the CMMWCNTs. As indicated by the values of Freundlich coefficient (K_F), the adsorption of LAS by the CMMWCNTs was stronger at higher temperature, probably due to the increased dispersive forces among dissolved LAS monomers and diffusion rate of LAS and decreased solution viscosity across the external boundary layer and also within the pores of CMMWCNTs.

3.3. Effects of aqueous solution composition

3.3.1. Effect of NaCl concentration

Effects of ionic strength with different cations were investigated to identify the governing factors of aqueous solution conditions for LAS adsorption on CMMWCNTs.

Fig. 5 shows the effect of NaCl concentration on LAS adsorption. It was found that the adsorption ability (q_e) of LAS onto the CMMWCNTs increased with increasing NaCl concentration in the range of 0–1.0 mol L⁻¹ and reached a maximum of 207 (C₁₀LAS), 258 (C₁₁LAS), 302 (C₁₂LAS), 329 (C₁₃LAS) mg g⁻¹, respectively. The increase of ionic strength may suppress the ionization of ionic surfactants in aqueous solution and enhance the hydrophobicity of LAS, which may result in the increase of the adsorption ability. Elevated concentration of electrolytes can also alter the solubility, surface activity, aggregation properties of surfactant, and thereby may affect the adsorption processes at the water-adsorbent interface, which could probably lead to the increase of surfactant adsorption [52]. Another reason may be that high ionic strength could probably reduce the electrical repulsion between adsorbed ionic surfactant molecules and thus enhance the adsorption when the equilibrium concentration is below the critical micelle concentration.

However, in a previous study with non-ionic organic compounds, their adsorption to CNTs was reported to be driven by a combined mechanism of hydrophobic effect and π - π electronic coupling with the surface of CNTs; in this study the ionic strength did not significantly modify the adsorption [53].

3.3.2. Effect of CaCl₂ and MgCl₂ concentration

The adsorption ability at equilibrium increased with increasing CaCl₂ and MgCl₂ concentration in the range from 0 to

Table 3
Estimated parameters by fitting Freundlich and Langmuir isotherm equation to the measured adsorption data of LAS on the CMMWCNTs (initial total LAS concentration 0–7000 mg L⁻¹; 0.05% (w/v) CMMWCNTs; pH 5.0; 0.1 mol L⁻¹ NaCl).

Temperature (°C)		Freundlich isotherm equation			Langmuir isotherm equation	
		K_F (L mg ⁻¹)	1/n	R^2	K_L (L mg ⁻¹)	R^2
25	C ₁₀ LAS	2.710	0.602	0.819	0.0002	0.040
	C ₁₁ LAS	4.449	0.550	0.833	0.0007	0.559
	C ₁₂ LAS	6.844	0.531	0.876	0.0015	0.869
	C ₁₃ LAS	6.887	0.558	0.848	0.0007	0.451
60	C ₁₀ LAS	9.168	0.696	0.906	0.0007	0.606
	C ₁₁ LAS	3.103	0.941	0.898	0.0007	0.591
	C ₁₂ LAS	10.836	0.760	0.931	0.0016	0.942
	C ₁₃ LAS	18.690	0.690	0.945	0.0026	0.978

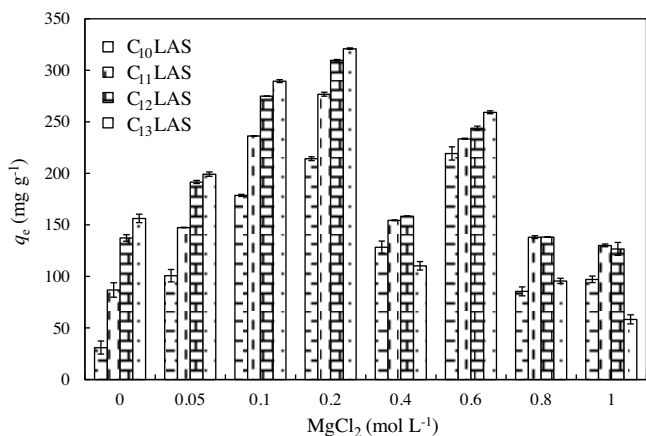


Fig. 7. Effect of MgCl₂ concentration on LAS adsorption to the CMMWCNTs (initial total LAS concentration 200 mg L⁻¹; 10 mL; 0.05% (w/v) CMMWCNTs; pH 5.0; equilibration time 300 min; agitation speed 200 rpm; 25 °C; results were average ± standard deviation of three replicates).

0.2 mol L⁻¹ while decreased when the CaCl₂ and MgCl₂ concentration increased from 0.2 to 1.0 mol L⁻¹ (Figs. 6 and 7).

There may be three reasons for the observed two-stage trend of LAS adsorption (q_e) on the CMMWCNTs with increasing CaCl₂ or MgCl₂ concentration. Firstly, the addition of CaCl₂ and MgCl₂ has the potential to precipitate the LAS and thus contribute to the increase of apparent adsorption at relatively low electrolyte concentration (<0.2 mmol L⁻¹); this agrees with a previous study was precipitates of anomalous solid particles was generated in the presence of small spherical micelles formed by complexation of 1,3-bis(*N*-dodecyl-*N*-propylsulfonate sodium)-propane (another anion surfactant) with calcium ion [54]. Secondly, it has been reported that divalent cations such as Ca²⁺ and Mg²⁺ can significantly reduce the solubility of anionic surfactants in aqueous solutions. For instance, Ca²⁺ ions, at concentrations beyond the CCC, mainly associate with the surfactant aggregates, thereby decreasing their solubility [54]. This may be a second reason that could partially explain our results for Ca²⁺ and Mg²⁺. Thirdly, as reported previously, divalent cations (Ca²⁺, Mg²⁺) can coagulate the stabilized single-walled CNTs (SWCNTs) at rather low concentrations (CCC: 0.20 and 0.31 mmol L⁻¹, respectively) while much higher concentrations of monovalent cations e.g. Na⁺ (CCC: 37 mmol L⁻¹) are needed for coagulating SWCNTs. CCC of SWCNTs is inversely related to the valency of the electrolyte counterions [55]. Similarly, in the present study, with increasing CaCl₂ concentration >0.2 mol L⁻¹, the observed decrease of LAS adsorption by the CMMWCNTs was probably due to the coagulation of the CMMWCNTs occurred and reduced solubility of LAS at high Ca²⁺ concentration (Figs. 6 and 7). A threshold concentration for CaCl₂ and MgCl₂ to achieve the max-

Table 4
Adsorption amount (q_e) and efficiency (X) of LAS on the CMMWCNTs in three different electrolytes at equilibrium (initial total LAS concentration 200 mg L⁻¹; 0.05% (w/v) CMMWCNTs; pH 5.0; 25 °C; concentration 0.1 mol L⁻¹).

LAS	NaCl		CaCl ₂		MgCl ₂	
	q_e (mg g ⁻¹)	X (%)	q_e (mg g ⁻¹)	X (%)	q_e (mg g ⁻¹)	X (%)
C ₁₀ LAS	224	56.1	316	79.0	214	53.6
C ₁₁ LAS	258	64.4	331	82.9	277	69.2
C ₁₂ LAS	302	75.5	297	74.2	310	77.4
C ₁₃ LAS	329	82.3	205	51.4	321	80.3

imum removal of LAS by the CMMWCNTs was observed to be 0.2 mol L⁻¹.

Contrastingly, a two-stage trend of LAS adsorption by the CMMWCNTs with increasing electrolyte concentration was not observed for the monovalent cation Na⁺ (Fig. 5).

The adsorption amount and efficiency of LAS on the CMMWCNTs in three different electrolytes (initial total LAS concentration 200 mg L⁻¹; 0.05% (w/v) CMMWCNTs; pH 5.0; 25 °C; concentration 0.1 mol L⁻¹) obtained at equilibrium in this study was summarized in Table 4. No distinct, consistent differences were observed between electrolytes or LAS homologues.

3.3.3. Effect of co-existing anions

The influence of sodium salts with different anions, which are often found in effluents, wastewater and natural water bodies, were investigated. The highest LAS adsorption was observed in sodium salt with a divalent anion (i.e., Na₂SO₄) (Fig. 8). At the same anion concentration of 0.8 mol L⁻¹, Na₂SO₄ solution showed higher ionic strength, which could reduce the electrostatic repulsion between CMMWCNTs particles and thus promote its suspension. In addition, the higher ionic strength could also “salt out” the LAS and thus facilitate the LAS adsorption [52]. Both mechanisms were reported by Paria and Khilar [52] and their synergy could explain the higher adsorption amount of LAS on CMMWCNTs in the presence of Na₂SO₄ when compared to the other three sodium salts.

3.3.4. Effect of temperature

The effect of temperature (25–60 °C) on adsorption amount at equilibrium is shown in Fig. 9. The observed increased adsorption of LAS with increasing temperature was partly due to the increased solubility of LAS at higher temperatures [56]. On the other hand, it has been reported that the adsorption of detergents on carbon black increased with increasing temperature, which was ascribed to the enhanced hydration of detergents [52,57]. The synergy of these two mechanisms could explain the observed greater adsorption ability (q_e) of LAS on the CMMWCNTs at higher temperature.

The findings of this study provide not only insights into the effects of electrolytes and temperature on LAS adsorption by CMMWCNTs but also useful information for the optimization of treatment processes for high salinity or warm wastewater and the

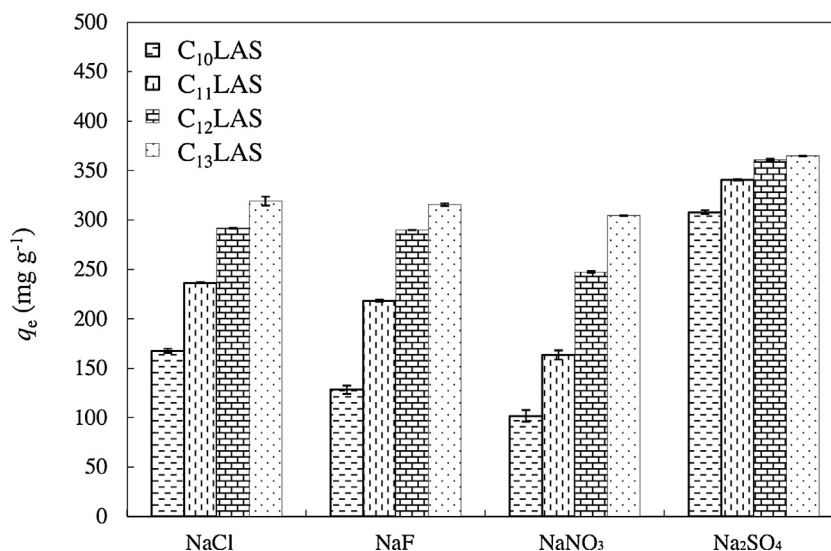


Fig. 8. Effect of co-existing anions of sodium salts on LAS adsorption on the CMMWCNTs (initial total LAS concentration 200 mg L^{-1} ; 10 mL ; 0.05% (w/v) CMMWCNTs; pH 5.0; equilibration time 300 min; agitation speed 200 rpm; 25°C ; results were average \pm standard deviation of three replicates).

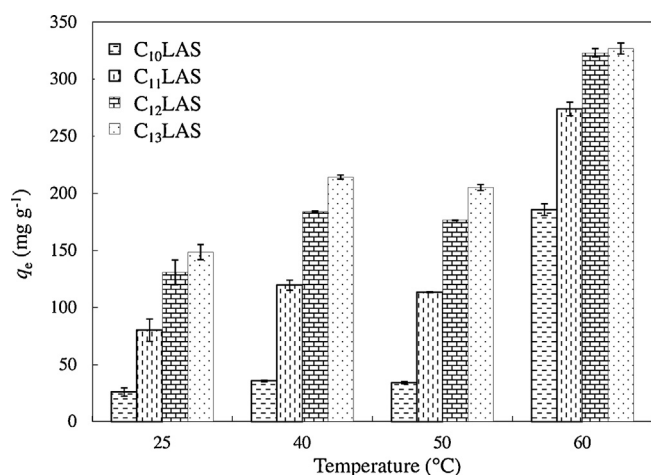


Fig. 9. Effect of temperature on LAS adsorption on the CMMWCNTs (initial total LAS concentration 200 mg L^{-1} ; 0.05% (w/v) CMMWCNTs; pH 5.0; equilibration time 300 min; agitation speed 200 rpm; 0.1 mol L^{-1} NaCl; results were average \pm standard deviation of three replicates).

prediction of the fate of anionic surfactants and nanotubes in brackish surface waters.

4. Conclusions

Results of the present study showed the kinetics of LAS adsorption on CMMWCNTs appeared to be rapid and followed a pseudo second-order kinetic at low initial LAS concentrations. The hydrophobic interaction and hydrogen bond interaction between LAS molecules and CMMWCNTs surface are acknowledged to strongly affect the adsorption behavior. The adsorption isotherm at 25°C and 60°C displayed different five-region modes probably due to the difference in the electrostatic repulsion force between LAS molecules and the hydration of LAS hydrophilic groups. The adsorption isotherm of LAS on CMMWCNTs was well described by the Freundlich model, indicating CMMWCNTs to have largely heterogeneous sorption surfaces. LAS sorption by CMMWCNTs was observed to be dependent upon both solution chemistry and temperature with the greatest adsorption of LAS being observed in the presence of sodium-divalent anion salts and at higher temperature.

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