Sorption of dodecyltrimethylammonium chloride (DTAC) to agricultural soils

CrossMark

Lei Xiang [a], Teng-Fei Sun [a], Mei-Jie Zheng [a], Yan-Wen Li [a], Hui Li [a], Ming-Hung Wong [a,b], Quan-Ying Cai [a], Ce-Hui Mo [a,*]

[a] Guangdong Provincial Research Center for Environment Pollution Control and Remediation Materials, School of Environment, Jinan University, Guangzhou 510632, China
[b] Consortium on Health, Environment, Education and Research (CHEER), Department of Science and Environmental Studies, Institute of Education, Tai Po, Hong Kong, China

HIGHLIGHTS

- DTAC sorption at low concentration was a physical process dominated by ion exchange.
- Soil clay contents acted as a predominant phase for DTAC sorption.
- DTAC sorption was affected by soluble ion with anion promotion and cation inhibition.

GRAPHICAL ABSTRACT
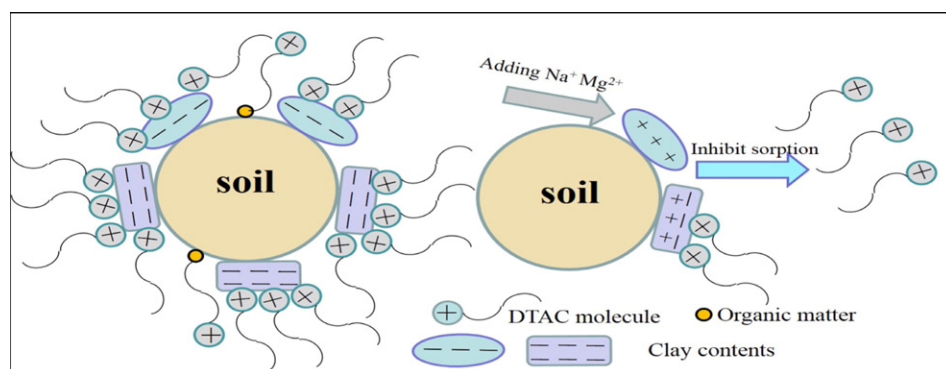
ABSTRACT

Quaternary ammonium compounds (QACs) used as cationic surfactants are intensively released into environment to be pollutants receiving more and more concerns. Sorption of dodecyltrimethylammonium chloride (DTAC), one of commonly used alkyl QACs, to five types of agricultural soils at low concentrations (1–50 mg/L) was investigated using batch experiments. DTAC sorption followed pseudo-second-order kinetics and reached reaction equilibrium within 120 min. Both Freundlich model and Langmuir model fitted well with DTAC isotherm data with the latter better. DTAC sorption was spontaneous and favorable, presenting a physical sorption dominated by ion exchanges. Sorption distribution coefficient and sorption affinity demonstrated that soil clay contents acted as a predominant phase of DTAC sorption. DTAC could display a higher mobility and potential accumulation in crops in the soils with lower clay contents and lower pH values. Sorption of DTAC was heavily affected by ions in solution with anion promotion and cation inhibition.

© 2016 Published by Elsevier B.V.

1. Introduction

Quaternary ammonium compounds (QACs) are a major class of cationic surfactants which have at least one hydrophobic hydrocarbon chain linked to a positively charged nitrogen atom (Jing et al., 2012).

* Corresponding author.
E-mail addresses: cai_quanying@yahoo.com (Q.-Y. Cai), tchmo@jnu.edu.cn (C.-H. Mo).

Due to surface activity and germicidal efficiency, QACs are extensively used in domestic, industrial, and agricultural applications (Zhang et al., 2015). The annual consumption of QACs was 500,000 tons in 2010 worldwide, and it is expected to increase continuously in the future (Zhu et al., 2010). As a result, QACs were inevitably released into various environmental compartments to be pollutants receiving more and more concerns in recent years (Zhang et al., 2015; Xiang et al., 2015). They have been frequently detected in water (μg/L to several mg/L), sludge (several hundreds, even thousands of mg/kg, dry weight (dw)), sediment (μg/kg to several mg/kg, dw), and soil (several mg/kg, dw) (Zheng et al., 2014; Ruan et al., 2014; Li et al., 2014; Pateiro-Moure et al., 2008a; Xiang et al., 2014).

QACs are recalcitrant to be biodegraded in the environment, especially in the anaerobic condition (Ruan et al., 2014; Li et al., 2014). They exert high toxicity to bacteria, invertebrate, algae, and fish with 50% effective concentrations (EC_{50}) in the range of 0.11 to 70 μmol/L (Nalecz-Jawecki et al., 2003). Furthermore, they can also cause genotoxic effects in mammalian and plant cells at environmentally relevant concentrations (1–10 mg/L) (Ferk et al., 2007). Meanwhile, the presence of QACs in the environment can increase the chance for induction and co-selection of antibiotic resistant bacterial, which is alarming for human health (Gaze et al., 2005; Tandukar et al., 2013). In addition, QACs play a great role in the bioavailability and mobility of the other pollutants coexisting in environment (Lu and Zhu, 2009; Liang et al., 2013). Therefore, there is a growing concern on the presence of QACs in the environment.

Sorption is a critical process controlling the mobility, bioavailability, and environmental fate of organic pollutants (Zhao et al., 2014). The ecological risks of organic pollutants are closely associated with their sorption behavior in the environment (Kim et al., 2012). Previous studies of QACs related to environmental fates were performed mainly in sewage treatment systems (Ying, 2006; Tezel et al., 2006; Ismail et al., 2010; Tezel et al., 2012). For example, Tezel et al. (2006) reported that the sorption of QACs to methanogenic bacteria culture at relatively higher concentrations (25–100 mg/L) decreased in the order of dodecyl > alkyl benzyl > octyl decyl > dioctyl and all the tested QACs were not degraded in the methanogenic conditions. Ismail et al. (2010) reported that the sorption of QACs at the concentrations of 50–300 mg/L in municipal sludge was dominated by hydrophobic interactions, and the sorption affinity of QACs positively correlated with their hydrophobicity, but negatively correlated with their critical micellar concentration (CMC).

QACs could be numerously released into farmland soil by land application of sewage sludge and usage of quaternary ammonium herbicides or irrigation water containing QACs (Pateiro-Moure et al., 2013; Warren, 2013; Xiang et al., 2015). In America, approximately 50% of municipal sludge is land-applied, leading to the accumulation of QACs in soil-crop system (Ismail et al., 2010). In China, QACs were also detected in both irrigation water (220 to 2000 μg/L) and agricultural soils (820 to 940 μg/kg, dw) (Zheng et al., 2014; Xiang et al., 2014). Crops can take up QACs from polluted irrigation water and soil, posing a potential threat to human health (Cao et al., 2014; Arrebola-Liébanas et al., 2014; Xiang et al., 2015). The sorption of QACs in soils plays a key role in their uptake, transfer and accumulation in crops. Previous studies have reported the sorption of quaternary ammonium herbicides such as diquat (DQ), paraquat (PQ), and difenzoquat (DFQ) in agricultural soils (Pateiro-Moure et al., 2007; Pateiro-Moure et al., 2009a; Pateiro-Moure et al., 2009b; Pateiro-Moure et al., 2010). However, little information is available on the sorption behavior of alkyl QAC commonly detected in environment, which is of great difference in chemical structure compared with the quaternary ammonium herbicides (heterocyclic structure), in agricultural soils (Ruan et al., 2014; Xiang et al., 2016). Although there are some previous studies reported the sorption of alkyl QACs (e.g., hexadecyltrimethylammonium, HDTMA) to soils, or pure clay system, or clay-rich subsoil, the QAC concentrations used in those studies were relatively high (72.9–883.3 mg/L, or 0.1–5 times

the cation exchange capacity), and the mechanisms and influence factors of the sorption remain unknown (Xu and Boyd, 1994; Xu and Boyd, 1995; Sheng et al., 1996a; Sheng et al., 1996b; Sarkar et al., 2010). Furthermore, these studies aimed to improve the sorption and remediation of chlorinated and neutral organic compounds in alkyl QAC modified soils/clays (Xu and Boyd, 1994; Xu and Boyd, 1995; Sheng et al., 1996a; Sheng et al., 1996b) other than the sorption of alkyl QAC to agricultural soils and the potential risk of alkyl QAC uptake by crops from soils (Pateiro-Moure et al., 2008b).

Dodecyltrimethylammonium chloride (DTAC) is one of commonly used alkyl QACs, and it has been detected in water (60–1600 μg/L) (Zheng et al., 2014), sewage sludge (22–103 mg/kg, dw) (Ruan et al., 2014), soil (210–360 μg/kg, dw) (Xiang et al., 2014), and vegetables (8.8–122 μg/kg, dw) (Xiang et al., 2015). Furthermore, DTAC is a homologue of alkyl QACs with shorter alkyl chains (alkyl chains C12), and higher mobility and toxicity (Berthelsen et al., 2000; Xiang et al., 2015). According to Jing et al. (2012), the EC_{50} values of DTAC for two green algae *Chlorella pyrenoidosa* and *Scenedesmus quadricauda* were 1.36 and 0.503 mg/L, respectively. In the present study, therefore, DTAC was selected as a representative at relatively lower concentrations (1–50 mg/L) to investigate the sorption of alkyl QAC to five different types of agricultural soils using batch equilibrium assays. Meanwhile, the effects of soil physicochemical characteristics on the sorption were evaluated by performing Pearson's correlations between the sorption isotherm parameters of DTAC and the soil components. The purpose of current study was to understand the sorption mechanism of alkyl QAC to agricultural soils, and to provide environmental implications in the aspect of fate and transport of alkyl QACs in crop-soil system.

2. Experimental

2.1. Materials

Five distinct and unpolluted agricultural surface soils (0–20 cm) labeled by soil A, soil B, soil C, soil D, and soil E were collected from Guangdong province, southern China. Soil A, soil B, and soil C were selected as representatives of submerged soil, while soil D and soil E represented the coastal saline soil and upland soil, respectively. All of the soil samples were freeze-dried, ground and sieved through a 2-mm stainless steel sieve, and then stored at 4 °C before use. The organic matter (OM), clay content, contents of phosphorus (P) and potassium (K), cation exchange capacity (CEC), and pH of the soils were measured according to recommended soil testing procedures (Lu, 2000). The results are provided in Table 1. DTAC with 99.9% purity was purchased from Aladdin (Seattle, USA). Deionized water was used for sorption experiments. The other reagents including potassium chloride (KCl), calcium chloride ($CaCl_2$), ferric chloride ($FeCl_3$), potassium sulfate (K_2SO_4), hydrochloric acid (HCl), and sodium azide (NaN_3) purchased from Guangzhou Chemicals Reagents Co. Ltd., China, were of analytical grade.

2.2. Batch sorption experiments

All of batch sorption experiments were performed according to OECD guideline 106 (OECD, 2000). Briefly, 1 g of the soil and 25 mL of DTAC solution (1–50 mg/L) were added to 50 mL of Teflon-lined centrifuge tubes. At the same time, 0.01 M $CaCl_2$ and 0.3% of NaN_3 were added to provide a constant ionic strength and inhibit microbial activities, respectively. After vortex-mixing for 30 s, the solution was shaken at 250 rpm and 25 ± 2 °C for 0–600 min and then centrifuged at 8000 rpm for 5 min. DTAC concentrations in supernatants were determined using liquid-liquid extraction and gas chromatography mass spectrometry (GC–MS) (Zheng et al., 2014). The adsorbed mass of DTAC in soils was calculated based on the concentration difference,

Table 1
Physicochemical properties of the tested agricultural soils.

Samples	pH	OMs[a] (%)	CEC[b] (cmol/kg)	Phosphorus (g/kg)	Potassium (g/kg)	Clay (%)	Silt (%)	Sand (%)
Soil A	4.8 (0.2)[c]	2.5 (0.1)	38.0 (0.8)	0.4 (0.0)	2.5 (0.1)	19.5 (0.6)	32.5 (0.8)	48.0 (1.4)
Soil B	3.6 (0.1)	5.1 (0.1)	122.0 (4.9)	0.2 (0.0)	7.9 (0.3)	27.3 (1.0)	20.7 (1.0)	52.0 (2.6)
Soil C	5.7 (0.2)	1.5 (0.1)	70.3 (2.8)	0.6 (0.0)	22.7 (1.1)	46.8 (2.1)	29.2 (1.0)	24.0 (1.4)
Soil D	5.9 (0.2)	5.2 (0.2)	114.0 (5.7)	1.0 (0.0)	19.5 (0.9)	31.2 (0.8)	44.8 (2.2)	24.0 (0.2)
Soil E	6.2 (0.2)	1.2 (0.1)	7.1 (0.4)	0.2 (0.0)	5.9 (0.2)	30.0 (0.8)	41.0 (1.6)	29.0 (1.1)

[a] Organic matter contents.
[b] Cation exchange capacity.
[c] Values in parentheses involved with the standard deviation (n = 3).

which can be expressed as:

$$q_t = (c_0 - c_{surf}) \cdot v/m \qquad (1)$$

where q_t is DTAC concentration (mg/g) in soils at sampling time, and c_0, c_{surf}, v, and m are the initial DTAC concentration (mg/L), DTAC concentration (mg/L) in solution at sampling time, total solution volume (mL), and soils mass (g), respectively. In the present study, v and m were 25 mL and 1 g, respectively. Preliminary experiments showed that DTAC loss could be negligible due to volatilization, microbial activity, and sorption by the centrifuge tube, as well as DTAC desorption from the original soils.

In the sorption kinetic assay, the initial concentration of DTAC was set as 50 mg/L. Supernatants were sampled at 15 time intervals (i.e., 1, 3, 6, 10, 20, 30, 40, 50, 60, 80, 100, 120, 150, 300 and 600 min). In the sorption isotherm assay, the initial concentrations of DTAC were set as 1, 5, 10, 20 and 50 mg/L, respectively. Supernatants were sampled for DTAC determination after 120 min of shaking, based on the sorption kinetic assays. Previous studies revealed that the sorption equilibrium time of organic compounds at a lower initial concentration was shorter than that at a higher initial concentration (Ismail et al., 2010). Thus, the sorption equilibrium time of DTAC at 50 mg/L was appropriate for use for that at lower concentrations (<50 mg/L). All of experiments were performed in triplicate.

2.3. Analytical methods

2.3.1. DTAC analysis

10 mL of supernatant was collected, adjusted the pH to 1 with HCl, and then extracted by chloroform twice with 5 mL each time. Both supernatants were combined and concentrated to 2 mL for GC–MS analysis. The analysis of DTAC in extract was conducted on a Shimadu-QP2010 Plus GC–MS with a DB-5MS fused silica capillary column (30 m length, 0.25 mm diameter, 0.1 μm film thickness). The injection amount was 1 μL in splitless mode. The carrier gas was high purity helium (99.9999%) at a flow rate of 1.0 mL/min. The temperatures of injector, detector and ion source were 280 °C, 250 °C, and 250 °C, respectively. The temperature of the column oven was set as follows: started at 100 °C (held 2 min), increased to 200 °C at 30 °C min^{-1}, increased to 280 °C (held 4 min) at 40 °C min^{-1}. The mass spectrometer was carried out by application of electron-impact (EI) mode (70 eV) in the selective ion monitoring (SIM) mode. The target ion of DTAC was 58, and its retention time was 5.31 min (Fig. 1). The limit of quantification (LOQ) for DTAC and its average recovery in supernatants of the tested soils were 8.3 μg/L and 92.6% ± 7.8%, respectively.

2.3.2. FTIR spectroscopy analysis

Two types of the tested soils were prepared and freeze-dried for FTIR analysis: (i) Soils with DTAC: 1 g of each soil in 50 mg/L of DTAC solution with 0.01 M CaCl$_2$ was shaken under 250 rpm at 25 ± 2 °C for 120 min. The saturated sorption of DTAC occurred under this condition according to the kinetic assay. (ii) Soils without DTAC: 1 g of soils in 0.01 M CaCl$_2$ solution was shaken under the same condition. The two types of samples were mixed with KBr at a ratio of 1.5:300, respectively, and then

ground and pressed into pellets for FTIR spectroscopy analysis. The FTIR spectra of samples were collected using the Nicolet Nexus 6700 FTIR spectrometer equipped with a Zn-Se horizontal ATR crystal and a triglycine sulfate detector. The scanning spectra were recorded from 400 to 4000 cm^{-1} with a scanning velocity of 1 cm^{-1}.

2.4. Data analysis

Data analyses including calculating average value, standard deviation (SD), regression and Pearson correlation were carried out by *SPSS* 21.0. The statistical significance was set at $P < 0.05$.

3. Results and discussion

3.1. Sorption kinetic model of DTAC to soils

The sorption process of DTAC to the agricultural soils could be divided into three stages (Fig. 2a). In the first stage (within 30 min), concentrations of DTAC adsorbed to soils increased rapidly over time. This stage was a rapid sorption phase concerning the ion exchange (Ismail et al., 2010). In the second stage (30 to 120 min), the amount of DTAC adsorbed to soils increased slowly over time. This stage was a slow sorption phase depending mainly on hydrophobic interactions (Ismail et al., 2010). In the third stage (>120 min), concentrations of DTAC to soils remained unchanged, presenting an equilibrium sorption phase.

The pseudo-second-order kinetics model has been frequently used to describe the three stages of the sorption kinetics of contaminants to
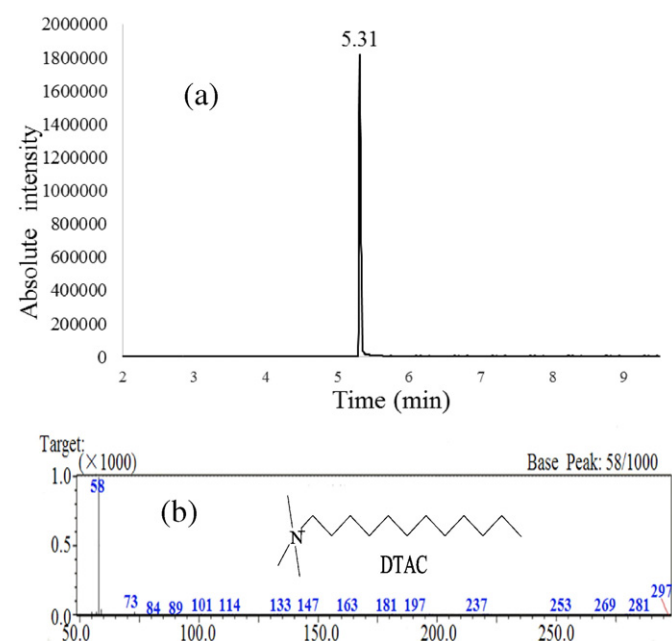

Fig. 1. Typical GC–MS chromatogram (a) and mass spectrum (b) of DTAC (1 mg/L).
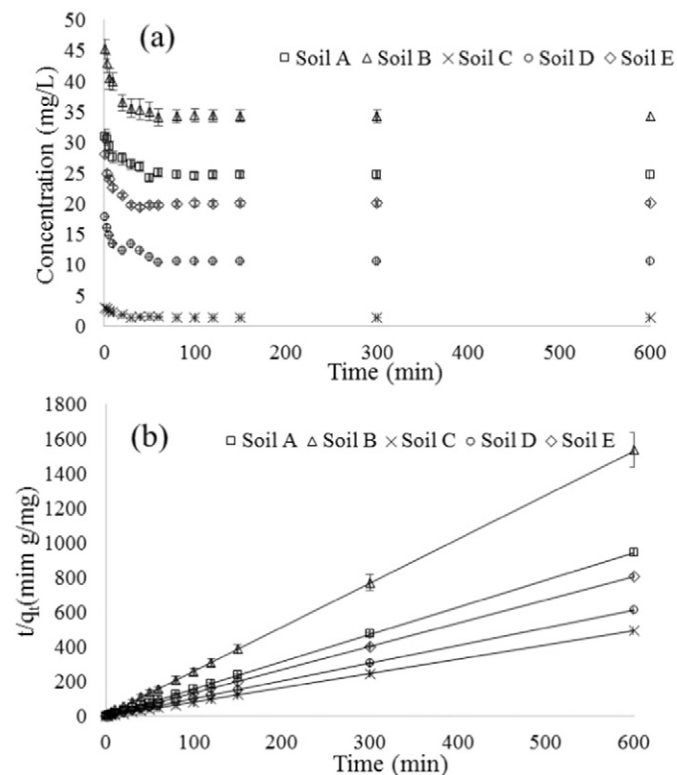
Fig. 2. Sorption kinetics of DTAC in the agricultural soils: (a) Relationships between the sampling time and the DTAC concentration in supernatants and (b) the pseudo-second-order model fit to DTAC sorption kinetics data.

sorbents (Fang et al., 2014). This model can be expressed as follows:

$$t/q_t = 1/(k \cdot q_e^2) + 1/q_e \cdot t \tag{2}$$

where t is sampling time (min), q_t is DTAC concentration (mg/g) in the agricultural soils at sampling time, k is pseudo-second-order rate constant, and q_e (mg/g) is DTAC concentration in soils at equilibrium time. In the present study, the sorption of DTAC to soils fitted the pseudo-second-order kinetics model with the coefficients of correlations (R^2) above 0.995 (Fig. 2b).

The sorption mechanism of DTAC to hydrophobic sorbent with a negative charge depended on ion exchange and hydrophobic interactions according to a previous study (Ismail et al., 2010). The DTAC head group ($-NH_2^+$) initially interacted with the negatively charged sites of the sorbent by replacing weakly binding cations on the sorbent surface, which occurred rapidly in the first phase. After the negatively charged sites of the sorbent were occupied, DTAC sorption proceeded via partitioning or hydrophobic forces between the alkyl chain ($-C_{12}H_{25}$) of DTAC and organic matter (OM) of the sorbent. This process was relatively slow, belonging to the slow sorption phase. Similarly, HDTMA was initially adsorbed by cation exchange and then by hydrophobic bonding in a vermiculite-rich subsoil (Xu and Boyd, 1995). After all active sites were occupied, the sorption of DTAC to soils was no longer observed, reaching the equilibrium sorption phase. Although involved a three-stage process, sorption of DTAC to the tested soils reached equilibrium within 120 min (Fig. 2), generally in agreement with those to municipal sludge (<4 h) (Ismail et al., 2010) and kaolinite (<2 h) (Jiang et al., 2011).

3.2. Sorption isotherm

Two commonly used isotherm models, Freundlich and Langmuir isotherms were used to assess the distribution of DTAC between liquid and solid phases in the present study. Freundlich model is frequently used to describe the equilibrium on heterogeneous surfaces, which was previously applied to describe QAC sorption to municipal sludge and methanogenic bacteria culture (Tezel et al., 2006; Ismail et al., 2010), while Langmuir model is often applied to describe monolayer sorption on a uniform surface (Wang et al., 2015). The linearized forms of Freundlich model and Langmuir model can be expressed as Eqs. (3) and (4), respectively:

$$\ln q_e = \ln k_F + n \cdot \ln c_e \tag{3}$$

$$1/q_e = 1/Q_m + 1/(Q_m \cdot k_L \cdot c_e) \tag{4}$$

where q_e has been defined in Eq. (2), c_e is DTAC concentration in solution at equilibrium time, k_F is Freundlich constant indicating affinity of a compound to a given sorbent [(mg/g)/(mg/L)^n], n is a dimensionless empirical parameter describing the linearity of a isotherm, which is convex, linear, and concave when $n < 1$, $n = 1$, and $n > 1$, respectively (Doretto et al., 2014), Q_m is maximum sorption capacity (mg/g), and k_L is Langmuir constant related to sorption binding energy (L/mg).

In the present study, DTAC sorption isotherm of the agricultural soils fitted well to Freundlich and Langmuir models with regression coefficients (R^2) > 0.960 and the latter better (Fig. 3, Table 2), indicating that DTAC sorption to the tested soils was monolayer-type. However, Ismail et al. noted that sorption of DTAC to primary, activated, and digested sludge was a multilayer sorption process (Ismail et al., 2010). These discrepant findings may be attributed to variation in DTAC concentrations. The sorption of surfactants or amphiphilic compounds was mediated mainly by ion exchange and hydrophobic interactions at the concentration below 0.01 of the critical micelle concentrations (CMC) (Ismail et al., 2010; Wang et al., 2015). In the absence of aggregation, hemi-micelles or micelles were unlikely to form, and the surfactants were adsorbed as a monomer to sorbents at the low concentration (<0.01 CMC) (Wang et al., 2015). When the concentration above 0.01 CMCs, hemi-micelles and even micelles (above CMC) formed, and thus the sorption of the surfactants were dominated by
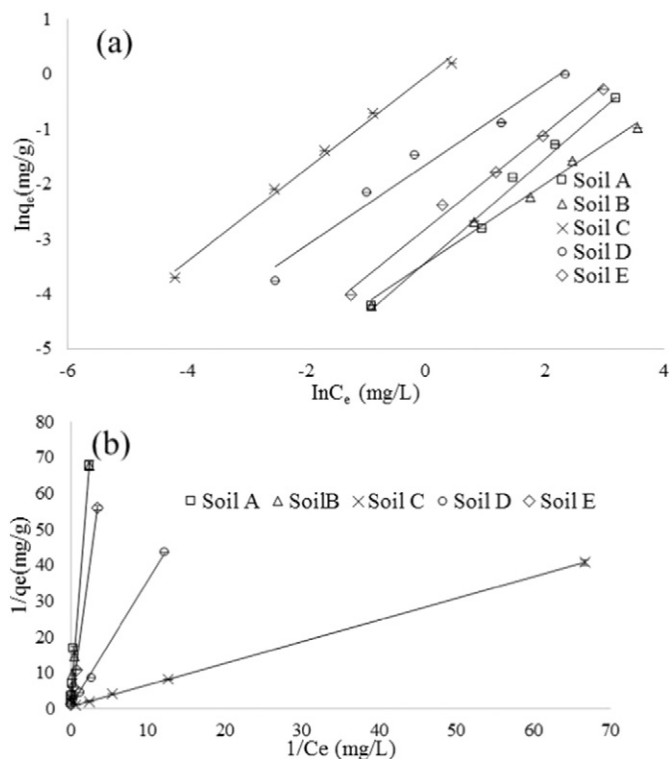

Fig. 3. Sorption isotherms of DTAC in the soils: (a) Freundlich sorption isotherms and (b) Langmuir sorption isotherms.

Table 2
Sorption isotherm parameters of DTAC sorption to soils.

Samples	Freundlich isotherm			Langmuir isotherm			ΔG^0 (kJ/mol)	K_d (L/g)	
	n	k_F (mg/g)/(mg/L)^n	R^2	k_L (L/mg)	Q_m (mg/g)	R^2		$c_e = 2$ mg/L	$c_e = 10$ mg/L
Soil A	0.946 (0.006)[a]	0.033 (0.003)	0.988 (0.001)	0.069 (0.002)	0.521 (0.025)	0.992 (0.001)	−23.9 (0.075)	0.031 (0.001)	0.021 (0.001)
Soil B	0.724 (0.001)	0.032 (0.001)	0.989 (0.001)	0.118 (0.002)	0.322 (0.012)	0.998 (0.000)	−25.3 (0.036)	0.031 (0.001)	0.017 (0.001)
Soil C	0.841 (0.003)	0.946 (0.014)	0.988 (0.010)	0.999 (0.049)	1.670 (0.030)	0.999 (0.000)	−30.6 (0.121)	0.556 (0.001)	0.152 (0.002)
Soil D	0.723 (0.008)	0.190 (0.004)	0.969 (0.001)	0.144 (0.008)	1.981 (0.040)	0.998 (0.000)	−25.8 (0.131)	0.222 (0.005)	0.117 (0.000)
Soil E	0.868 (0.004)	0.060 (0.002)	0.993 (0.000)	0.027 (0.002)	2.372 (0.100)	0.999 (0.000)	−21.6 (0.209)	0.060 (0.002)	0.050 (0.001)

[a] Values in parentheses involved with the standard deviation (n = 3).

hydrophobic interactions and exhibited a multilayer sorption process (Ismail et al., 2010). The CMC of DTAC has been reported at around 5.5 mg/L (Ismail et al., 2010). In the present study, the DTAC concentrations were all below 55 mg/L (0.01 CMC of DTAC), without the generation of hemi-micelles or critical micelles, and thus its sorption favored a monolayer over a multilayer process which was observed in the higher DTAC concentrations (50 to 300 mg/L) used previously (Ismail et al., 2010).

The n values ranging from 0.723 to 0.946 in Freundlich model for the agricultural soils indicated a slightly nonlinear DTAC sorption isotherm. By comparing previous study, the n values involved with DTAC sorption on both municipal sludge (0.48 to 0.83) and methanogenic bacteria culture (0.25 to 0.42) were generally lower than the values measured in the present study (Tezel et al., 2006; Ismail et al., 2010). This difference is attributed to the more complex components of sorbents that contained lots of organic matters (1365 to 1800 mg/L COD), smaller colloidal solids, volatile solid (1 to 2.2 g/L), and high ionic strength used in the previous study (Tezel et al., 2006; Ismail et al., 2010), which may have enhanced the heterogeneities of the sorbents and decreased the linearity of DTAC isotherms. As for the k_F values, these values in the present study ranged between 0.032 and 0.946 [(mg/g)/(mg/L)^n], being generally lower at least by an order of magnitude than those for municipal sludge (0.95 to 3.14 [(mg/g)/(mg/L)^n]). This indicated that the affinity of DTAC to adsorb on the agricultural soils was much lower than on the municipal sludge (Table 2), which are ascribed to the municipal sludge rich in organic matters and the higher DTAC concentration (50 to 300 mg/L) used in the previous study (Ismail et al., 2010).

The Q_m values and k_L values in the Langmuir model for the agricultural soils ranged from 0.322 to 2.372 mg/g and from 0.027 to 0.999 L/mg, respectively (Table 2). Based on further analysis of the Langmuir equation, the dimensionless parameter of sorption intensity (R_L) could be calculated from the following Eq. (5):

$$R_L = 1/(1 + k_L \cdot c_0) \tag{5}$$

where k_L and c_0 have been defined above in Eq. (4) and Eq. (1), respectively.

The R_L value is recommended to demonstrate whether this sorption will be favorable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$) or irreversible ($R_L = 0$) (Wu et al., 2010; Lei et al., 2013). In the present study, the R_L values varied from 0.020 to 0.974 under the initial concentrations of DTAC between 1 and 50 mg/L (Supplementary data, Table S1), indicating DTAC sorption to the agricultural soils was favorable. Thermodynamic information for DTAC sorption can be measured through the changes in standard Gibbs free energy (ΔG^0), which can be expressed as the following Eq. (6):

$$\Delta G^0 = -RT \ln k_L \tag{6}$$

where R is gas constant (8.314 J/kmol), T is sorption temperature (K), and k_L is Langmuir constant (L/mol). In the present study, T is 298.15 K. As shown in Table 2, all the ΔG^0 values were negative and ranged from −21.6 to −30.6 kJ/mol (Table 2), indicating the

spontaneous nature and feasibility of the DTAC sorption process to the agricultural soils. Generally, the ΔG^0 value in the range of −20 to 0 kJ/mol indicates a physical sorption, while this value between −80 and −400 kJ/mol indicates a chemisorption (Wu et al., 2010; Lei et al., 2013). Therefore, the ΔG^0 data in the present study suggested that the sorption of DTAC to the agricultural soils might be mainly a physical sorption. To further distinguish chemical or physical sorption of the DTAC adsorbed to the agricultural soils, Dubinin-Radushkevich (D-R) isotherm model was also applied for fitting the DTAC isotherm data. Based on the D-R model, the mean sorption energy (E, kJ/mol) was calculated, which can be used to distinguish whether this sorption is a physical process ($0 < E < 8$ kJ/mol) or a chemical process ($8 < E < 16$ kJ/mol) (Lei et al., 2013). The linearized D-R model and the E value can be expressed as Eqs. (7) and (8), respectively:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{7}$$

$$E = 1/(2 \cdot \beta)^{0.5} \tag{8}$$

where q_e is defined in Eq. (2), q_m is the maximum sorption of the adsorbate at the total specific micropore volume of the sorbent (mg/g), β is the activity coefficient involved to E value (mol^2/J^2), and ε is the Polanyi potential which can be expressed as $\varepsilon = RT\ln(1 + 1/c_e)$ (Wu et al., 2010). According to the Supplementary data, Table S2, the DTAC isotherm data fitted to the D-R model, with the R^2 values of 0.708–0.923. Although these R^2 values in D-R model were slightly lower than those in Freundlich and Langmuir model, they were still acceptable as to calculation of the E values. All of E values in the present study ranged from 1.284 to 3.912 kJ/mol, indicating that the physical nature of DTAC sorption to the agricultural soils. This conclusion was also supported by the fact that no significant differences were observed in the sorption bands in FTIR spectra between the tested soils, with and without DTAC (Supplementary data, Fig. S1).

3.3. Effects of soil components on DTAC sorption

To compare DTAC sorption to the various agricultural soils, the single-point sorption partition coefficient (K_d) at a specific concentration, a good indicator of evaluating sorption capacity (Kim et al., 2012; Zhang et al., 2013), was obtained based on the fitting results of Langmuir isotherms. K_d values (L/g) can be expressed as the following equation:

$$K_d = q_e/c_e \tag{9}$$

where q_e and c_e are the parameters mentioned before. Two c_e values (2, 10 mg/L) close to the environmentally relevant concentration of DTAC were given in the present study. The K_d values for the tested agricultural soils were calculated between 0.031 and 0.556 at $c_e = 2$ mg/L, and between 0.017 and 0.152 g/L at $c_e = 10$ mg/L, respectively (Table 2). The K_d values at the two given c_e had significant positive correlations with contents of soil clay and potassium ($R^2 > 0.868$) (Table 3), which indicated DTAC tended to be adsorbed on the agricultural soils with higher contents of clays and potassium (e.g., soil C and soil D). This suggestion

Table 3
The correlation coefficients (R^2) for sorption isotherm parameters and the soil physicochemical properties.

Parameters	k_L	Q_m	E	k_F	n	K_d2[b]	K_d10	ΔG
pH	0.207	0.940[*a]	0.456	0.332	0.230	0.417	0.621	0.012
OMs	− 0.364	− 0.384	− 0.214	− 0.390	− 0.799	− 0.284	− 0.153	− 0.017
CEC	0.104	− 0.361	0.198	0.064	− 0.858[*]	0.146	0.180	− 0.462
Phosphorus	0.271	0.358	0.588	0.349	− 0.345	0.513	0.727	− 0.461
Potassium	0.749	0.437	0.934[*]	0.797	− 0.467	0.890[*]	0.953[*]	− 0.822
Clay	0.896[*]	0.485	0.930[*]	0.924[*]	− 0.216	0.931[*]	0.868[*]	− 0.786
Silt	− 0.270	0.780	0.076	0.139	0.075	0.002	0.327	0.343
Sand	− 0.468	− 0.913[*]	− 0.737	− 0.581	0.106	− 0.685	− 0.869[*]	0.334

[a] The statistically significant correlation was marked with "*" ($n = 5$).
[b] The K_d2 and K_d10 were K_d values when Ce values were at 2 and 10 mg/L, respectively.

was further confirmed by the fact that significant positive correlation was observed between the mean sorption energy (E) and contents of soil clay and potassium ($R^2 > 0.930$). Furthermore, both the k_F values related to sorption affinity and the k_L values involved to sorption binding strength had significant positive correlations with contents of clay contents ($R^2 > 0.896$). Generally, soil clay minerals have a high specific surface area and high negative charge, and thus they can usually adsorb organic pollutants, especially those containing cations (Yuan et al., 2014). A previous study showed that the major factor governing the sorption of the quaternary ammonium herbicide (DQ) was the solid state organic fraction with the clay mineral contents (Pateiro-Moure et al., 2008b). Furthermore, alkyl QAC (HDTMA) favored to be adsorbed to clay and formed HDTMA-clay complexes in the clay or the clay-rich soil (Xu and Boyd, 1994; Xu and Boyd, 1995; Gao et al., 2001). Therefore, the soils with higher contents of clay had stronger sorption binding strength for DTAC. However, only ammonium ion head (N^+—) in DTAC molecule with a long chain (—$C_{12}H_{25}$) reduced the cation exchange between DTAC itself and the cations adsorbed to soil clays due to steric hindrance. Thus, DTAC molecules tended to preferentially exchange with low-valence ions such as K^+ other than high-valence ions during DTAC sorption process. This is supported by the fact that the tested soils with higher contents of potassium had stronger sorption capacities to DTAC, but no significant positive correlation between DTAC sorption capacity and CEC values was observed.

Besides clay contents and potassium contents, other physicochemical properties of the tested soils also affected DTAC sorption. The Q_m values related to maximum sorption capacity had a positive correlation with pH values of the tested soils ($R^2 = 0.940$) (Table 3), which was attributable to the increase in active sorption sites with negative charges with increasing pH values. Furthermore, the n values as indicative of isotherm linearity were negatively correlated with soil CEC values, which may be related to the heterogeneities of the tested soils increasing with the rising CEC values.

3.4. Effects of ions on DTAC sorption

In order to further estimate the effects of ions on DTAC sorption, the sorption isotherm assays of DTAC, using soil C as an example, were performed by batch sorption experiments in the presence of common ions (K^+, Ca^{2+}, Fe^{3+}, Cl^-, and SO_4^{2-}) in water solution at 0.1 mol/L. Both K^+ and Cl^- were prepared from KCl, while Ca^{2+}, Fe^{3+}, and SO_4^{2-} were

prepared from $CaCl_2$, $FeCl_3$, and K_2SO_4, respectively. The results showed that DTAC sorption isotherm in the presence of ions also fitted Langmuir model with regression coefficients $R^2 > 0.997$ (Table 4). Under an identical anion (Cl^-) background, the values of isotherm parameters including k_L, Q_m, and K_d at two given concentration c_e (2 and 10 mg/L) decreased in the order of: blank solution (without adding ions) > K^+ solution > Ca^{2+} solution > Fe^{3+} solution. These values in Cl^- solution were lower than those in SO_4^{2-} solution under an identical cation (K^+) background (Table 4). These results indicated that anions promoted DTAC sorption, cations inhibited DTAC sorption, and the effects of both cations and anions on DTAC sorption increased with their valence. Previous researches reported anion (SO_4^{2-}, Br^-, Cl^-) increased the sorption of alkyl QAC (HDTMA) (Xu and Boyd, 1995) to a clay-rich subsoil while cation (Cu^{2+}) decreased the sorption of quaternary ammonium herbicides (PQ, DQ, and DFQ) in vineyard soils (Pateiro-Moure et al., 2007). The difference in influences on DTAC sorption between cations and anions further proved that the sorption mechanisms of DTAC at low concentrations to the soils were dominated by ion exchanges. Cations adsorbed to the soil surfaces competed with DTAC for the negatively charged sites and thus decreased DTAC sorption capacity. In contrast, the absorbed anions offset the electronegativity of the soils and thus promoted DTAC sorption. However, the values of isotherm parameters (k_L, Q_m, and K_d) in SO_4^{2-} solution were lower than those in solution without adding ions. This unexpected result was attributed to the fact that SO_4^{2-} and K^+ coexisted in the SO_4^{2-} solution prepared from K_2SO_4, and the sorption capacity of K^+ ions to soil surfaces was greater than SO_4^{2-} ion because the soil surfaces carried net negative charges. Besides inorganic ions, organic ions can also affect the QAC sorption. Pateiro-Moure et al. (2010) reported that divalent quaternary ammonium herbicides (e.g., PQ and DQ) could interfere each other's sorption in vineyard soils.

4. Conclusions

Sorption of DTAC to five agricultural soils at low concentrations (1–50 mg/L) reached equilibrium rapidly (within 120 min). Sorption kinetics of DTAC followed pseudo-second-order kinetics. Isotherm data of DTAC sorption were fitted with both Freundlich and Langmuir models with the latter better. The models exercised and the FTIR spectroscopy demonstrated that a spontaneous and favorable physical sorption dominated by ion exchange was the sorption mechanism of DTAC at low

Table 4
Langmuir sorption isotherm parameters of DTAC under common ions (K^+, Ca^{2+}, Fe^{3+}, Cl^- and SO_4^{2-}) in water.

Ions	Q_m (mg/g)	K_L (L/mg)	R^2	K_d2[a]	K_d10
Without ions	1.670 (0.030)[b]	0.999 (0.009)	0.999 (0.000)	0.556 (0.001)	0.152 (0.002)
K^+(Cl^-)	1.403 (0.028)	0.129 (0.009)	0.999 (0.000)	0.148 (0.002)	0.081 (0.000)
Ca^{2+}	1.133 (0.034)	0.121 (0.001)	0.997 (0.000)	0.111 (0.004)	0.062 (0.002)
Fe^{3+}	0.858 (0.036)	0.106 (0.008)	0.997 (0.000)	0.074 (0.001)	0.044 (0.000)
SO_4^{2-}	1.871 (0.025)	0.138 (0.003)	0.997 (0.000)	0.202 (0.004)	0.108 (0.002)

[a] The K_d2 and K_d10 were K_d values when ce values were at 2 and 10 mg/L, respectively.
[b] Values in parentheses involved with the standard deviation ($n = 3$).

concentrations. DTAC sorption was affected by soil components and the sorption increased with increasing soil clay contents. DTAC sorption was also affected by ions in solution with anion promotion and cation inhibition. The mean DTAC sorption energy (1.286 to 3.912 kJ/mol) was relatively low and the sorption proceeded by physical sorption. Therefore, the sorption affinity of DTAC, one of alkyl QACs commonly used, to agricultural soils was lower, displaying a higher mobility and potential accumulation in crops grown in the soils with lower clay contents and lower pH values. Given the higher mobility and potential bioaccumulation of alkyl QACs in agricultural soils, investigations on the source, occurrence, fate, and risk assessment of alkyl QACs in soil-crop system are urgently needed.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.03.235.

References

Arrebola-Liébanas, F.J., Abdo, M.A.H., Moreno, J.L.F., Martínez-Vidal, J.L., Frenich, A.G., 2014. Determination of quaternary ammonium compounds in oranges and cucumbers using QuEChERS extraction and ultra-performance liquid chromatography/tandem mass spectrometry. J. AOAC Int. 97, 1021–1026.

Berthelsen, P., Beltoft, V., Thorup, I., Søborg, I., Nielsen, E., 2000. Toxicological Evaluation and Limit Values for 2-ethylhexyl Acrylate, Propylene Carbonate, Quaternary Ammonium Compounds, Triglycidyl Isocyanurate and Tripropyleneglycol Diacrylate. Danish Veterinary and Food Administration, Glostrup, Denmark.

Cao, H.W., Kang, M.Q., Chen, Z., Li, L.L., Cui, M.H., Chen, M.Y., Zhang, H.Q., Wang, Y.H., 2014. Determination of five quaternary ammonium compounds in foodstuffs using high performance liquid chromatography-tandem mass spectrometry. Anal. Methods 6, 4790–4796.

Doretto, K.M., Peruchi, L.M., Rath, S., 2014. Sorption and desorption of sulfadimethoxine, sulfaquinoxaline and sulfamethazine antimicrobials in Brazilian soils. Sci. Total Environ. 476–477, 406–414.

Fang, C.R., Long, Y.Y., Shen, D.S., 2014. Sorption behavior of dibutyl phthalate and dioctyl phthalate by aged refuse. Environ. Sci. Pollut. Res. 21, 7641–7649.

Ferk, F., Misik, M., Hoelzl, C., Uhl, M., Fuerhacker, M., Grillitsch, B., Parzefall, W., Nersesyan, A., Micieta, K., Grummt, T., Ehrlich, V., Knasmüller, S., 2007. Benzalkonium chloride (BAC) and dimethyldioctadecyl-ammonium bromide (DDAB), two common quaternary ammonium compounds, cause genotoxic effects in mammalian and plant cells at environmentally relevant concentrations. Mutagenesis 22, 363–370.

Gao, B., Wang, X., Zhao, J., Zhao, J.C., Sheng, G.Y., 2001. Sorption and cosorption of organic contaminant on surfactant-modified soils. Chemosphere 43, 1095–1102.

Gaze, W.H., Abdouslam, N., Hawkey, P.M., Wellington, E.M., 2005. Incidence of class 1 integrons in a quaternary ammonium compound-polluted environment. Antimicrob. Agents Chemother. 49, 1802–1807.

Ismail, Z.Z., Tezel, U., Pavlostathis, S.G., 2010. Sorption of quaternary ammonium compounds to municipal sludge. Water Res. 44, 2303–2313.

Jiang, H., Xu, L., Hu, Y., Wang, D., Li, C., Meng, W., Wang, X.J., 2011. Flotation and adsorption of quaternary ammonium cationic collectors on diaspore and kaolinite. T. Nonferr. Metal. SOC 21, 2528–2534.

Jing, G., Zhou, Z., Zhuo, J., 2012. Quantitative structure-activity relationship (QSAR) study of toxicity of quaternary ammonium compounds on Chlorella pyrenoidosa and Scenedesmus quadricauda. Chemosphere 86, 76–82.

Kim, Y., Lim, S., Han, M., Cho, J., 2012. Sorption characteristics of oxytetracycline, amoxicillin, and sulfathiazole in two different soil types. Geoderma 97, 185–186.

Lei, C., Hu, Y., He, M., 2013. Adsorption characteristics of triclosan from aqueous solution onto cetylpyridinium bromide (CPB) modified zeolites. Chem. Eng. J. 219, 361–370.

Li, X.L., Luo, X.J., Mai, B.X., Liu, J.Q., Chen, L., Lin, S.S., 2014. Occurrence of quaternary ammonium compounds (QACs) and their application as a tracer for sewage derived pollution in urban estuarine sediments. Environ. Pollut. 185, 127–133.

Liang, Z.J., Ge, F., Zeng, H., Xu, Y., Peng, F., Wong, M.H., 2013. Influence of cetyltrimethyl ammonium bromide on nutrient uptake and cell responses of Chlorella vulgaris. Aquat. Toxicol. 138, 81–87.

Lu, R.K., 2000. Analytical Methods of Soil And Agri-chemistry. third ed. Scientific and Technology Press, Bei Jing.

Lu, L., Zhu, L.Z., 2009. Reducing plant uptake of PAHs by cationic surfactant-enhanced soil retention. Environ. Pollut. 157, 1794–1799.

Nalecz-Jawecki, G., Grabinska-Sota, E., Narkiewicz, P., 2003. The toxicity of cationic surfactants in four bioassays. Ecotoxicol. Environ. Saf. 54, 87–91.

OECD, 2000. OECD guidelines for testing of chemicals, test guideline 106: adsorption-desorption using a batch equilibrium method Paris.

Pateiro-Moure, M., Pérez-Novo, C., Arias-Estevez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., 2007. Influence of copper on the adsorption and desorption of paraquat, diquat, and difenzoquat in vineyard acid soils. J. Agric. Food Chem. 55, 6219–6226.

Pateiro-Moure, M., López-Periago, E., Arias-Estevez, M., Simal-Gándara, J., 2008a. Determination of quaternary ammonium herbicides in soils: comparison of digestion, shaking and microwave-assisted extractions. J. Chromatogr. A 1196, 110–116.

Pateiro-Moure, M., Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., 2008b. Occurrence and downslope mobilization of quaternary ammonium herbicide residues in vineyard-devoted soils. Bull. Environ. Contam. Toxicol. 80, 407–411.

Pateiro-Moure, M., Pérez-Novo, C., Arias-Estevez, M., Rial-Oterob, R., Simal-Gándara, J., 2009a. Effect of organic matter and iron oxides on quaternary herbicide sorption–desorption in vineyard-devoted soils. J. Colloid Interface Sci. 333, 431–438.

Pateiro-Moure, M., Nóvoa-Muñoz, J.C., Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., 2009b. Quaternary herbicides retention by the amendment of acid soils with a bentonite-based waste from wineries. J. Hazard. Mater. 164, 769–775.

Pateiro-Moure, M., Arias-Estevez, M., Simal-Gándara, J., 2010. Competitive and non-competitive adsorption/desorption of paraquat, diquat and difenzoquat in vineyard-devoted soils. J. Hazard. Mater. 178, 194–201.

Pateiro-Moure, M., Arias-Estevez, M., Simal-Gandara, J., 2013. Critical review on the environmental fate of quaternary ammonium herbicides in soils devoted to vineyards. Environ. Sci. Technol. 47, 4984–4998.

Ruan, T., Song, S.J., Wang, T., Liu, R.Z., Lin, Y.F., Jiang, G.B., 2014. Identification and composition of emerging quaternary ammonium compounds in municipal sewage sludge in China. Environ. Sci. Technol. 48, 4289–4297.

Sarkar, B., Megharaj, M., Xi, Y., Krishnamurti, G.S.R., Naidu, R., 2010. Sorption of quaternary ammonium compounds in soils: implications to the soil microbial activities. J. Hazard. Mater. 184, 448–456.

Sheng, G., Xu, S., Boyd, S.A., 1996a. Mechanism(s) controlling sorption of neutral organic contaminants by surfactant-derived and natural organic matter. Environ. Sci. Technol. 30, 1553–1557.

Sheng, G., Xu, S., Boyd, S.A., 1996b. Cosorption of organic contaminants from water by hexadecyltrimethylammonium-exchanged clays. Water Res. 30, 1483–1489.

Tandukar, M., Oh, S., Tezel, U., Konstantinidis, K.T., Pavlostathis, S.G., 2013. Long-term exposure to benzalkonium chloride disinfectants results in change of microbial community structure and increased antimicrobial resistance. Environ. Sci. Technol. 47, 9730–9738.

Tezel, U., Pierson, J.A., Pavlostathis, S.G., 2006. Fate and effect of quaternary ammonium compounds on a mixed methanogenic culture. Water Res. 40, 3660–3668.

Tezel, U., Tandukar, M., Martinez, R.J., Sobecky, P.A., Pavlostathis, S.G., 2012. Aerobic biotransformation of n-tetradecylbenzyldimethylammonium chloride by an enriched Pseudomonas spp. community. Environ. Sci. Technol. 46, 8714–8722.

Wang, F., Shih, K., Leckie, J.O., 2015. Effect of humic acid on the sorption of perfluorooctane sulfonate (PFOS) and perfluorobutane sulfonate (PFBS) on boehmite. Chemosphere 118, 213–218.

Warren, 2013. Quaternary ammonium compounds can be abundant in some soils and are taken up as intact molecules by plants. New Phytol. 198, 476–485.

Wu, Y., He, J., Yang, L., 2010. Evaluating adsorption and biodegradation mechanisms during the removal of microcystin-RR by periphyton. Environ. Sci. Technol. 44, 6319–6324.

Xiang, L., Zheng, M.J., Wang, X.K., Li, Y.W., Mo, C.H., Cai, Q.Y., Huang, X.P., Wu, X.L., Zhao, H.M., 2014. Simultaneous extraction and determination of three quaternary ammonium compounds in soil by ultrasonic exaction and gas chromatography–mass spectrometry. Chin. J. Anal. Chem. 42, 1459–1464.

Xiang, L., Wang, X.K., Li, Y.W., Huang, X.P., Wu, X.L., Zhao, H.M., Li, H., Cai, Q.Y., Mo, C.H., 2015. Analysis of trace quaternary ammonium compounds (QACs) in vegetables using ultrasonic-assisted extraction and gas chromatography mass spectrometry. J. Agric. Food Chem. 63, 6689–6697.

Xiang, L., Sun, T.F., Mo, C.H., Li, Y.W., Cai, Q.Y., Li, H., 2016. Environmental problems and research progresses of quaternary ammonium compounds (QACs). Prog. Chem. http://dx.doi.org/10.7536/PC151129.

Xu, S., Boyd, S.A., 1994. Cation exchange chemistry of hexadecyltrimethylammonium in a subsoil containing vermiculite. Soil Sci. Soc. Am. J. 58, 1382–1391.

Xu, S., Boyd, S.A., 1995. Cationic surfactant sorption to a vermiculitic subsoil via hydrophobic bonding. Environ. Sci. Technol. 29, 312–320.

Ying, G., 2006. Fate, behavior and effects of surfactants and their degradation products in the environment. Environ. Int. 32, 417–431.

Yuan, G.L., Qin, J.X., Jun, L., Lang, X.X., 2014. Persistent organic pollutants in soil near the Changwengluozha glacier of the Central Tibetan Plateau, China: their sorption to clays and implication. Sci. Total Environ. 472, 309–315.

Zhang, Q., Yang, C., Huang, W., Dang, Z., Shu, X., 2013. Sorption of tylosin on clay minerals. Chemosphere 93, 2180–2186.

Zhang, C., Cui, F., Zeng, G.M., Jiang, M., Yang, Z.Z., Yu, Z.G., Zhu, M.Y., Shen, L.Q., 2015. Quaternary ammonium compounds (QACs): a review on occurrence, fate and toxicity in the environment. Sci. Total Environ. 518-519C, 352–362.

Zhao, L.X., Bian, J.N., Zhang, Y.H., Zhu, L.Y., 2014. Comparison of the sorption behaviors and mechanisms of perfluorosulfonates and perfluorocarboxylic acids on three kinds of clay minerals. Chemosphere 114, 51–58.

Zheng, M.J., Xiang, L., Li, Y.W., Mo, C.H., Cai, Q.Y., Huang, X.P., Wu, X.L., Zhao, H.M., 2014. Simultaneous extraction and determination of three quaternary ammonium compounds in water using liquid-liquid exaction and gas chromatography–mass spectrometry. Chin. J. Anal. Chem. 42, 735–740.

Zhu, M., Ge, F., Zhu, R., Wang, X., Zheng, X., 2010. A DFT-based QSAR study of the toxicity of quaternary ammonium compounds on Chlorella vulgaris. Chemosphere 80, 46–52.