



Effect of salinity on formaldehyde interaction with quartz sand and kaolinite colloid particles: batch and column experiments

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Abstract

Formaldehyde (FA) is a highly reactive compound that is used extensively in medicine, agriculture and industrial processes as a disinfectant for killing bacteria and fungi. Therefore, the probability of FA release in the environment, with subsequent surface and ground water contamination is significant. In this study, the effect of salinity on the interaction of FA with quartz sand and kaolinite colloid particles under static and dynamic conditions was examined. Emphasis was given to salinity fluctuations, as related to typical saltwater intrusion cases commonly encountered in coastal cultivated agricultural lands. All bench scale experiments were performed under controlled conditions at room temperature. The data from the batch experiments were adequately fitted with a linear sorption isotherm. The transport of FA through columns packed with quartz sand under different salinity concentrations was also investigated. Formaldehyde was analyzed spectrophotometrically according to the Hantzsch reaction. The results of this study indicated that FA has a weak affinity for sand, but a relatively strong affinity for kaolinite colloid particles. Salinity was shown to have minor effects on FA transport.

Keywords Formaldehyde · Salinity · Sorption · Quartz sand · Kaolinite · Transport · Porous media

Introduction

Pesticide contamination of soils and water bodies is an important environmental issue, which has been extensively explored by numerous investigators (Maggia et al. 2012; Boesten 2016; Kaur et al. 2016; Gevao et al. 2000). Thousands of substances are used as pesticides. For example, formaldehyde (FA) is a disinfectant, fungicide or bactericide, which is frequently used for the surface sterilization of plant seeds (Tomlin 2000; Yuan et al. 2015). In agriculture, FA is often used as a 37–40% w/v solution in water, known as formalin. Formaldehyde is also used in many different applications due to its high reactivity, stability, purity in commercial form, and low cost (Lotfy and Rashed 2002). Formaldehyde is also used in aquaculture industry to prevent external parasites, and to threat fungal infections (Bills et al. 1977; Lalonde et al. 2015). Industrial manufactories

that produce or utilize FA usually generate wastewater containing significant concentrations of this compound, ranging from a few to hundreds of milligrams per liter (Afkhami et al. 2011). All of these applications can lead to FA releases in the environment. Therefore, it is not surprising that FA is the most commonly found aldehyde in the environment (Liteplo et al. 2002). Trace levels of FA have been detected in several water samples (Hill et al. 2009). Concentrations of FA up to 30 µg/L have also been detected in ozonated drinking water (Li et al. 2008). Due to its high solubility, FA has also been observed in natural rain, clouds, fog, steam, and soil (Heimlich 2008).

Formaldehyde is a polar, volatile and highly reactive organic compound with pungent odor, with undesirable adverse health effects (Yu et al. 2014). Formaldehyde is classified as human carcinogen, because it may cause nasopharyngeal cancer and possibly leukemia (IARC 2006). Formaldehyde is highly toxic to bacteria and other pathogens (TURI 2013). Exposure to FA can also cause central nervous system damage, blood, immune system and developmental disorders, as well as blindness, and respiratory disease (Afkhami et al. 2011). In general, due to its potential adverse health effects, FA is not well suited for use as a fungicide to control plant diseases (Yuan et al. 2015). Therefore,

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standards have been set to limit human exposure and health risk. The US Environmental Protection Agency (US EPA 2006) has established a maximum daily dose reference for FA of 0.2 mg/kg per day.

The fate and mobility of contaminants in subsurface formations are controlled mainly by sorption processes. Clay minerals, such as kaolinite, are important components of soil, and they are instrumental in transporting contaminants in soil and sediments (Li et al. 2010; Liu et al. 2011; Behera et al. 2010, 2012; Wu et al. 2013; Chrysikopoulos et al. 2017). Kaolinite is abundant in many near-surface geological environments, and it is highly sorptive due to its small particle size, large surface area, and chemically active surface defect sites (Polati et al. 2006; Vasconcelos and Bunker 2007; Konduri and Fatehi 2017). Colloids, including clay minerals such as kaolinite, could change the fate and mobility of many types of contaminants. Under certain environmental conditions, colloid particles could carry sorbed contaminants over long distances in the subsurface environment and pose a significant threat to surface and ground water quality. Contaminant transport can significantly be enhanced by colloids when the sorption process is irreversible, and colloid concentrations are high (National Research Council 2003.) Several experimental investigations have demonstrated the enhanced migration of contaminants during co-transport of contaminants and suspended colloids (Grolimund et al. 1996; Karathanasis 1999; de Jonge et al. 2004; Chen et al. 2015; Syngouna and Chrysikopoulos 2015, 2016; Xing et al. 2015; Syngouna et al. 2017).

Salinity can influence the sorption behavior of contaminants (Green-Ruiz 2008; Chen et al. 2011; Zhang and Huang 2011; Oh et al. 2016). Additionally, salinity can affect contaminant sorption by changing the electrical state of the sorbent surfaces (Higgins and Luthy 2006; Jeon et al. 2011). Soil salinization, due mainly to human activities, is one of the major soil degradation threats in coastal areas (Daliakopoulos et al. 2016). The salinity of agricultural lands is caused mainly by continuous application of irrigation waters with high-salt concentration (Geeson et al. 2002), and by the use of fertilizers (Moreira Barradas et al. 2014). Soil salinity can cause serious damage to soil structure and reduction of soil fertility. High concentrations of some soluble salts can be toxic to crop growth and can also hinder the absorption of other mineral nutrients (Geeson et al. 2002). Salinity effects are more important in sandy soils, because they naturally have larger pores that allow for relatively rapid drainage (Moreira Barradas et al. 2014).

A series of laboratory batch sorption and column experiments were conducted in this study to determine the effect of salinity fluctuations on FA fate and transport, as related to typical salt-water intrusion cases commonly encountered in coastal cultivated agricultural lands. To our knowledge, no previous study has examined the sorption behavior of FA

onto quartz sand or kaolinite under salinity fluctuations, as well as the transport behavior of FA through columns packed with quartz sand.

Procedures

Materials and methods

A 1000 mg/L FA stock solution was prepared by adding 124 μ L of 37 wt% FA solution (Sigma–Aldrich $\geq 99\%$) to a 50 mL volumetric flask with a piston pipette, and diluted to volume with distilled deionized water (ddH₂O). Standard working solutions were prepared by dilution of the stock solution with ddH₂O and addition of appropriate amount of NaCl. The standard working solutions were stored prior to use in the dark, at 4 °C (US EPA 1996). All experimental work with FA was performed in a fume hood.

Several approaches are available for the detection of FA (Rivero and Topiwala 2004; Li et al. 2008; Kenessov et al. 2011; Shin and Lim 2011). Most of these methods require chemical reaction of FA with various reagents to form colored derivatives, which can be observed spectrophotometrically (Jones et al. 1999; Michels 2001; Tsai et al. 2003a, b; Soman et al. 2008; Peng et al. 2014). The most common derivatizing agents are dinitrophenylhydrazine (DNPH) (Lehotay and Hromulakova 1994; Jones et al. 1999; Tsai et al. 2003a, b; Peng et al. 2014, US EPA 1996, 1998), and the Nash reagent (Nash 1953). In this study, FA was analyzed using the Nash method, which has been widely used, and the color of the resulting complex is measured with UV–visible spectroscopy (Jones et al. 1999; Kaszycki and Koloczek 2000; Economou and Mihalopoulos 2002; Eiroa et al. 2004; Seyfioglu et al. 2006; Zhen et al. 2007; Chanarat and Benjakul 2013).

The Nash reagent was prepared by dissolving 15 g of ammonium acetate, 0.3 mL of acetic acid, and 0.2 mL of acetyl acetone in ddH₂O to make 100 mL of reagent solution, which was stored in a brown bottle. The Nash reagent was mixed with an equal volume of solution containing FA at a maximum concentration of 8 mg/L. A yellow colored product, diacetyl dihydrolutidine (DDL), was formed by the reaction of Nash reagent with FA, which was determined by spectrophotometry at 412 nm (Nash 1953).

Various standard FA solutions (8, 6, 4, 3, 2, 1 mg/L) were prepared by diluting appropriate volumes of the FA stock solution (1000 mg/L). For each 5 mL of standard FA solution, 5 mL of the Nash reagent were added. These mixtures were used to measure DDL concentrations in duplicates. The absorbance of each sample was measured using a UV–Vis spectrophotometer (Shimadzu, UV-1900) at a wavelength of 412 nm). Finally, a calibration curve of peak area versus FA concentration was constructed by linear regression.

Quartz sand

Quartz sand was employed in this study, because quartz is the most common mineral found on the surface of the earth (Chrysikopoulos and Aravantinou 2014). The grain diameter of quartz sand used was in the range 0.425–0.600 mm (sieve no. 30/40), obtained with the procedures reported by Chrysikopoulos and Aravantinou (2014). The chemical composition of the quartz sand was: 96.2% SiO₂, 1.75% Al₂O₃, 0.78% K₂O, 0.46% Fe₂O₃, 0.15% Na₂O, 0.11% CaO, 0.06% SO₃, 0.03% P₂O₅, 0.02% BaO, 0.02% MgO, 0.01% Mn₃O₄, and 0.28% loss on ignition, as reported by the manufacturer (Filcom, Netherlands). The quartz sand was cleaned following well-established procedures (Chrysikopoulos and Aravantinou 2012; Fountouli and Chrysikopoulos 2018). Briefly, the sand was cleaned with 0.1 M HNO₃ (70%) for a period of 3 h, rinsed with ddH₂O, soaked in 0.1 M NaOH for 3 h, and subsequently rinsed again with ddH₂O. Finally, the sand was dried and sterilized at 80 °C.

Kaolinite

Kaolinite powder (KGa-1b, well crystallized kaolin, from Washington County, Georgia), purchased from Clay Minerals Society (Columbia, MO, USA), was used to make a colloidal kaolinite suspension (Pruett and Webb 1993). Only the < 2 µm KGa-1b fraction was used in this study, which was separated by sedimentation (Chrysikopoulos et al. 2017), and was purified following procedures described by Rong et al. (2008). Briefly, 12.5 g of KGa-1b were mixed with 50 mL distilled deionized water (ddH₂O) in a 1 L beaker. Sufficient (about 5–10 mL) hydrogen peroxide (30% solution), was added to oxidize the organic matter, while the pH was adjusted to 10 with 0.1 M NaOH. The suspension was diluted to 1 L and the < 2 µm colloid fraction was separated by sedimentation for a time period of 1 h. The size of the colloids was confirmed using a ZetaSizer analyzer (Nano ZS90, Malvern). The separated colloid suspension was flocculated with the addition of a 1 M NaCl solution. The colloid particles were washed with ddH₂O and ethanol and dried at 60 °C. The initial KGa-1b concentration, $C_{\text{KGa-1b}}$ [M/L³], used for the batch experiments was $C_{\text{KGa-1b}} = 100$ mg/L. The zeta potential and hydrodynamic diameter of the suspended KGa-1b particles were determined to be 1.81 mV and 1833 nm, respectively, based on triplicate measurements conducted with a ZetaSizer analyzer. Although significant variations may exist in zeta potential and hydrodynamic diameter of suspended KGa-1b particles, these values are in general agreement with published values (Yukselen and Kaya 2013; Syngouna and Chrysikopoulos 2013; Sun et al. 2016).

Batch experiments

Static and dynamic batch experiments were performed under controlled conditions at room temperature, to examine the interaction of FA with quartz sand or kaolinite. Three different FA concentrations (3, 5 and 8 mg/L) as well as four different salt concentrations (0, 1, 2 and 3 g/L NaCl) were examined. It should be noted that FA concentrations in the range 0.9–7.1 mg/L have been observed in environmental systems (Lalonde et al. 2015). Additionally, the range of NaCl concentrations used in this study was similar to the range employed by Oh et al. (2016). All batch experiments were performed in 20 mL Pyrex glass screw-cap tubes (Fisher Scientific). The tubes were washed with detergent, rinsed in ddH₂O, autoclave sterilized, and oven dried at 80 °C overnight. For the dynamic batch experiments the tubes were attached to a tube rotator (Selecta, Agitador orbit), which was operated at 12 rpm, to allow the sand or kaolinite to mix within the FA solution with the appropriate NaCl concentration.

For each experiment with quartz sand, 11 glass tubes were employed. The glass tubes contained 14 mL of FA solution with the appropriate NaCl concentration and 14 g of sand. All glass tubes were filled to the top. One tube was selected for analysis and removed from the pack randomly at several pre-determined time intervals. This 7-day time-period was shown to be sufficient for the FA-sand systems to reach equilibrium. Similarly, FA sorption onto kaolinite was conducted using glass tubes filled with 10 mL of sorbent solution (100 mg/L kaolinite) and 10 mL of FA solution with the appropriate NaCl concentration. One tube was selected for analysis and removed from the pack randomly at several pre-determined time intervals.

A liquid sample collected from each tube was centrifuged at 4000 rpm for 15 min (Rotofix, 32A, Hettich), to remove sand or kaolinite particles. Exactly 5 mL of the supernatant were added to 5 mL of Nash reagent and the resulting mixture was analyzed by UV–visible spectroscopy.

Column experiments

Column experiments were conducted to investigate the effect of salt concentration on the transport behavior of FA in a column packed with quartz sand. The glass column was 30 cm long with 2.5 cm inside diameter. For each experiment, the column was packed wet with quartz sand under vibration to minimize any layering. The column was saturated vertically with ddH₂O injected from the bottom of the column to remove any air pockets. Then the column was set horizontally. A peristaltic pump was used to control the flow in the column at the constant specific discharge of 1 mL/min. First, ddH₂O was pumped through the column for about 2 h to remove impurities. Then, four pore volumes (PV) of

FA solution (2 mg/L) with the appropriate NaCl concentration was injected into the column at the same flow rate, and subsequently the column was flushed with 3 PVs of ddH₂O. Effluent from the column was collected at certain interval times. To each one of the effluent samples collected an equal volume of Nash reagent was added, and the resulting mixtures were analysed by UV–visible spectroscopy.

Three sets of FA transport experiments were conducted with 0, 1, and 3 g/L NaCl solutions and a flow rate of $Q=1$ mL/min. The experimental conditions of each column experiment are listed in Table 3.

Theoretical considerations

Sorption

The sorption of FA onto solids (quartz sand or kaolinite) at equilibrium was successfully described by a simple linear isotherm model:

$$C_{\text{eq}}^* = K_d C_{\text{eq}}, \quad (1)$$

where C_{eq} [M_{FA}/L^3] is the concentration of the FA at equilibrium, in units of [mg FA/mL], C_{eq}^* [M_{FA}/M_s] is the concentration of the FA sorbed onto the adsorbent at equilibrium, in units of [mg FA/g solids], and K_d [L^3/M_p] is the distribution coefficient, in units of [mL/mg FA]. Note that M_{FA} represents the mass of FA, and M_s the mass of solids (quartz sand or kaolinite). The equilibrium concentration of FA sorbed onto quartz sand or kaolinite was determined in units of [mg FA/g solids] as follows:

$$C_{\text{eq}}^* = \frac{(C_0 - C_{\text{eq}}) V}{W}, \quad (2)$$

where C_0 [M_{FA}/L^3] is the initial liquid-phase FA concentration, in units of [mg FA/L], C_{eq} [M_{FA}/L^3] is the liquid-phase FA concentration at equilibrium, in units of [mg FA/L], V [L^3] is the solution volume, and W [M_s] is the dry mass of the adsorbent, in units of [g solids].

Fig. 1 Effect of initial FA concentration on kinetic sorption onto quartz sand under: (a–c) static conditions, and (d–f) dynamic conditions. Three different initial FA concentrations were examined: **a, b** $C_{\text{FA}(0)}=3$ mg/L, **c**, **d** $C_{\text{FA}(0)}=5$ mg/L, and **(e, f)** $C_{\text{FA}(0)}=8$ mg/L, at 23 °C

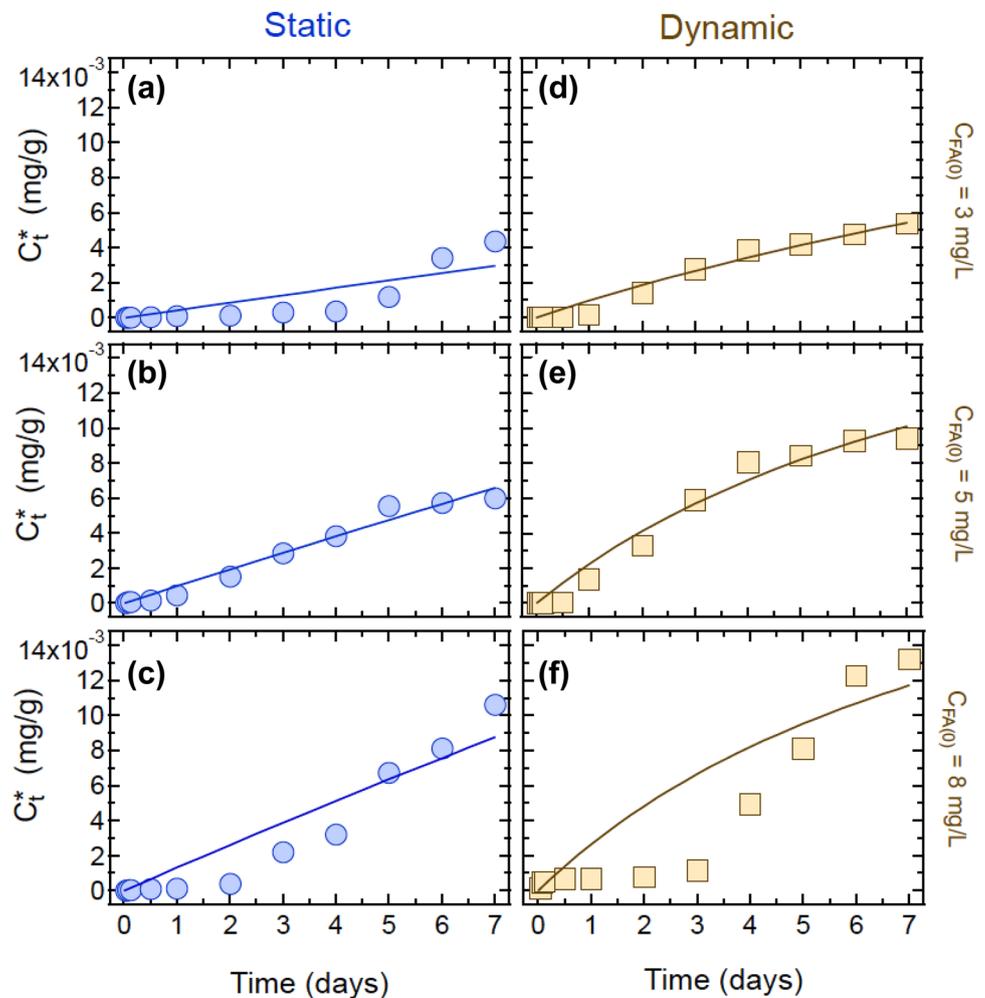


Fig. 2 Effect of salinity on kinetic sorption of FA ($C_{FA(0)} = 2 \text{ mg/L}$) onto quartz sand under: (a–c) static conditions, and (d–f) dynamic conditions. Three different concentrations of NaCl were examined: (a, b) 1 g/L, (c, d) 2 g/L, and (e, f) 3 g/L, at 23 °C

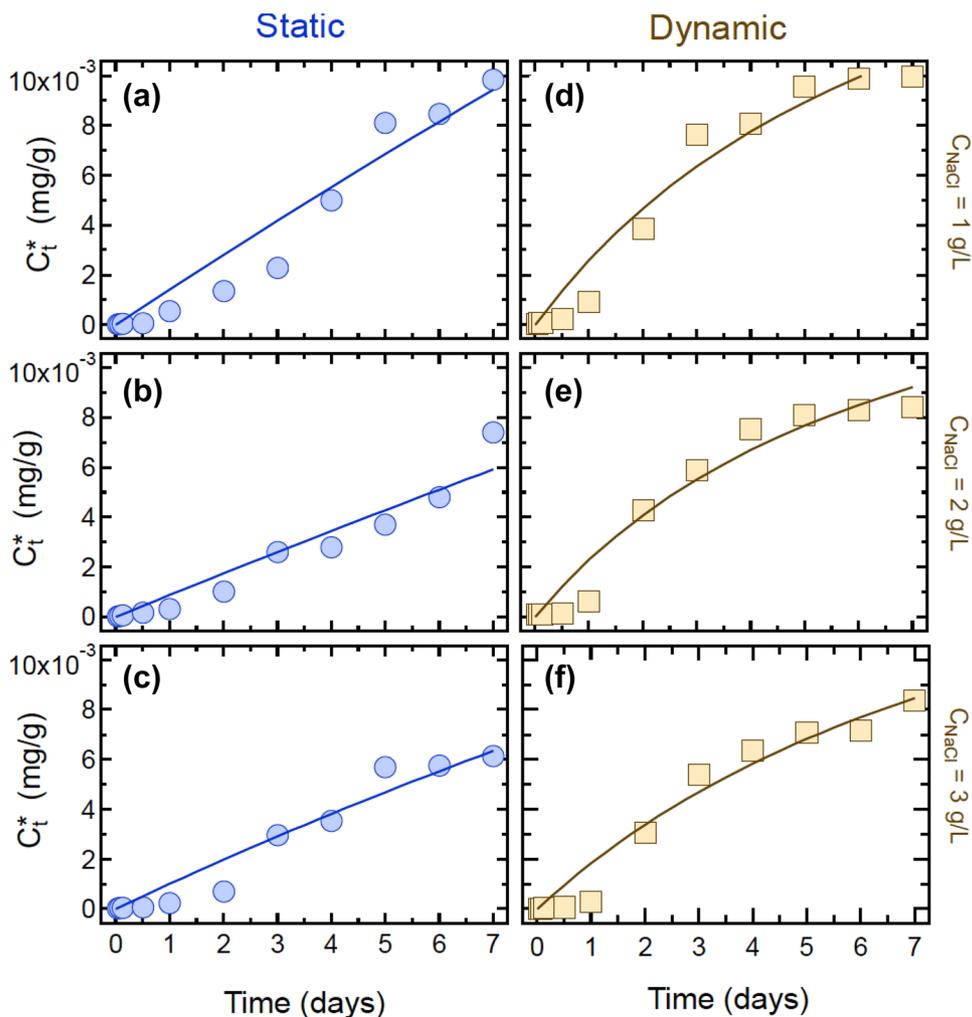


Table 1 Fitted parameters for FA sorption onto quartz sand (kinetic pseudo-second order sorption model)

$C_{FA(0)}$ (mg/L)	C_{NaCl} (mg/L)	k_{p2} (g sand/(mg FA·d))	C_{eq}^* (mg FA/g sand)
Static			
2	1	0.165	0.053
2	2	0.049	0.135
2	3	0.358	0.054
3	0	0.054	0.090
5	0	0.046	0.147
8	0	0.056	0.154
Dynamic			
2	1	5.735	0.023
2	2	7.685	0.019
2	3	4.490	0.021
3	0	1.762	0.024
5	0	4.292	0.024
8	0	3.945	0.027

The sorption kinetics data were best fitted with a pseudo-second-order kinetics model (Tsai et al. 2003a, b; Ho 2006; Wu et al. 2013):

$$\frac{dC_t^*}{dt} = k_{p2} (C_{eq}^* - C_t^*)^2 \Rightarrow C_t^* = \frac{(C_{eq}^*)^2 k_{p2} t}{1 + C_{eq}^* k_{p2} t}, \tag{3}$$

where $t[t]$ is time, $C_t^* [M_{FA}/M_s]$ is the concentration of the FA sorbed onto the soil at time t , and $k_{p2} [M_s/(M_{FA} \cdot t)]$ is the rate constant of the pseudo-second order sorption model. It should be noted that the pseudo-second-order kinetic sorption model has been employed in numerous sorption studies of environmental interest (Vasiliadou and Chrysikopoulos 2011; Upadhyayula et al. 2009; Sotirelis and Chrysikopoulos 2017), and is used to describe physicochemical interactions such as chemisorption (Ho 2006; Wu et al. 2013).

Fig. 3 Equilibrium sorption isotherms under: **a, b** static, and **d, e** dynamic conditions. The NaCl concentrations examined were: **a, c** $C_{NaCl}=0$ g/L, **b, d** $C_{NaCl}=3$ g/L. The slope of each fitted solid line is equal to K_d

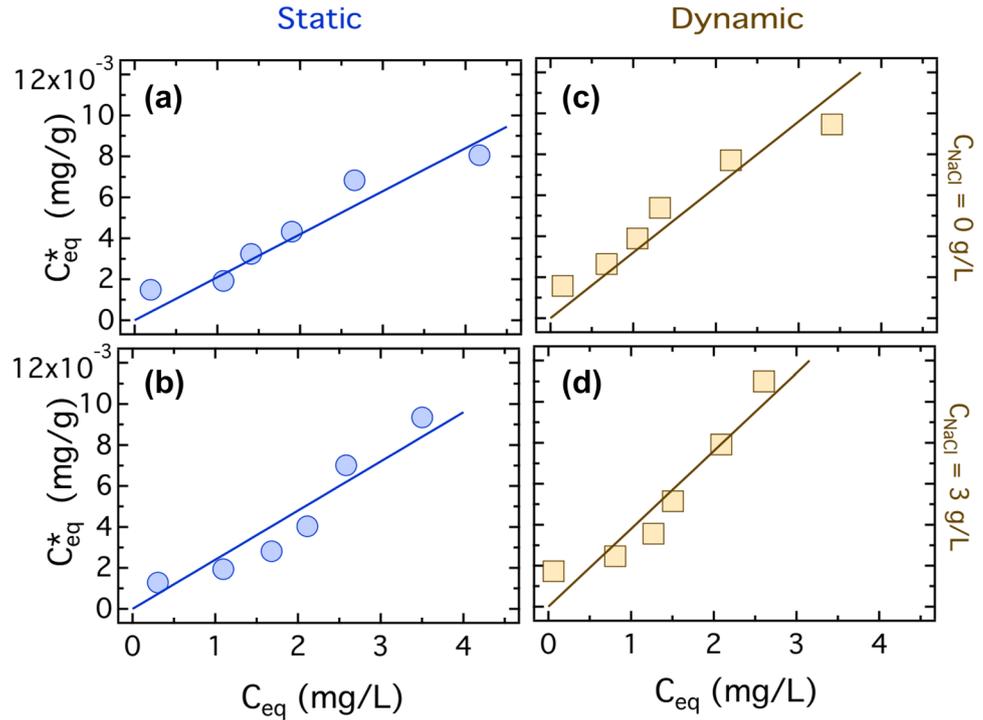


Table 2 Parameter values for equilibrium FA sorption onto quartz sand (linear isotherm model)

Experimental conditions	NaCl (mg/L)	K_d (L/mg)	R^2
Quartz sand			
Static	0	0.0021	0.90
Dynamic	0	0.0032	0.88
Static	3	0.0024	0.90
Dynamic	3	0.0038	0.91
Kaolinite			
Static	0	21.5	0.99
Dynamic	0	23.7	0.92
Static	3	28.7	0.92
Dynamic	3	31.9	0.90

Transport modeling

The transport of FA through one-dimensional, homogeneous porous media is governed by the following partial differential equation (Sim and Chrysikopoulos 1995):

$$\frac{\partial C_{FA}(t, x)}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial C_{FA}^*(t, x)}{\partial t} = -U \frac{\partial C_{FA}(t, x)}{\partial x} + D \frac{\partial^2 C_{FA}(t, x)}{\partial x^2}, \tag{4}$$

where C_{FA} [M_{FA}/L^3] and C_{FA}^* [M_{FA}/M_s] are the aqueous phase concentration and solid phase concentration of FA, respectively, t [t] is time, x [L] is the Cartesian coordinate,

ρ_b [M_s/L^3] is the dry bulk density, θ [-] is the porosity of the porous medium, U [L/t] is the interstitial velocity, and D [L^2/t] is the hydrodynamic dispersion coefficient. The second accumulation term in Eq. 4 can be described as follows (Sim and Chrysikopoulos 1999):

$$\frac{\rho_b}{\theta} \frac{\partial C_{FA}^*(t, x)}{\partial t} = r_f C_{FA}(t, x) - r_r \frac{\rho_b}{\theta} C_{FA}^*(t, x) \tag{5}$$

where r_f [$1/t$] is the rate coefficient of FA sorption onto quartz sand, and r_r [$1/t$] is the rate coefficient of FA desorption from quartz sand.

For a broad pulse type of source, the appropriate initial and boundary conditions are:

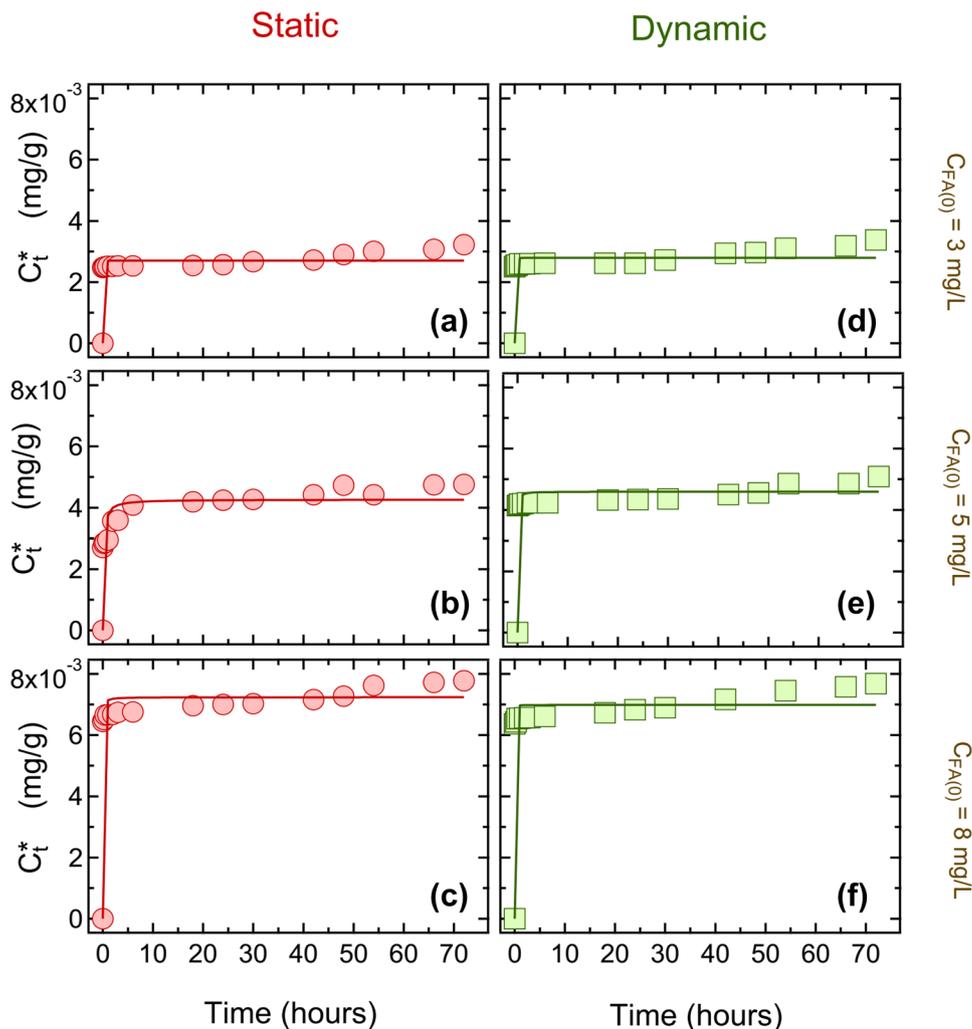
$$C_{FA}(0, x) = 0 \tag{6}$$

$$-D \frac{\partial C_{FA}(t, 0)}{\partial x} + UC_{FA}(t, 0) = \begin{cases} UC_{FA(0)}, & t \leq t_p \\ 0, & t > t_p \end{cases} \tag{7}$$

$$\frac{\partial C_{FA}(t, \infty)}{\partial x} = 0, \tag{8}$$

where $C_{FA(0)}$ is the source concentration, and t_p is the duration of solute pulse. Condition (6) establishes that there is no initial FA concentration within the porous medium. The flux-type boundary condition (7) for a broad pulse injection implies FA concentration discontinuity at inlet and preserves conservation of mass (Chrysikopoulos et al. 1990).

Fig. 4 Effect of initial FA concentration on kinetic sorption onto kaolinite particles under: **a–c** static conditions, and **d–f** dynamic conditions. Three different initial FA concentrations were examined: **a, b** $C_{FA(0)} = 3$ mg/L, **c, d** $C_{FA(0)} = 5$ mg/L, and **e, f** $C_{FA(0)} = 8$ mg/L, at 23 °C



The analytical solution to the transport model (4) and (5), subject to conditions (6)–(8) has been developed by Sim and Chrysikopoulos (1995).

The mass recovery (M_r [%]) of the injected FA is quantified by the following equation (Chrysikopoulos and Katzourakis 2015):

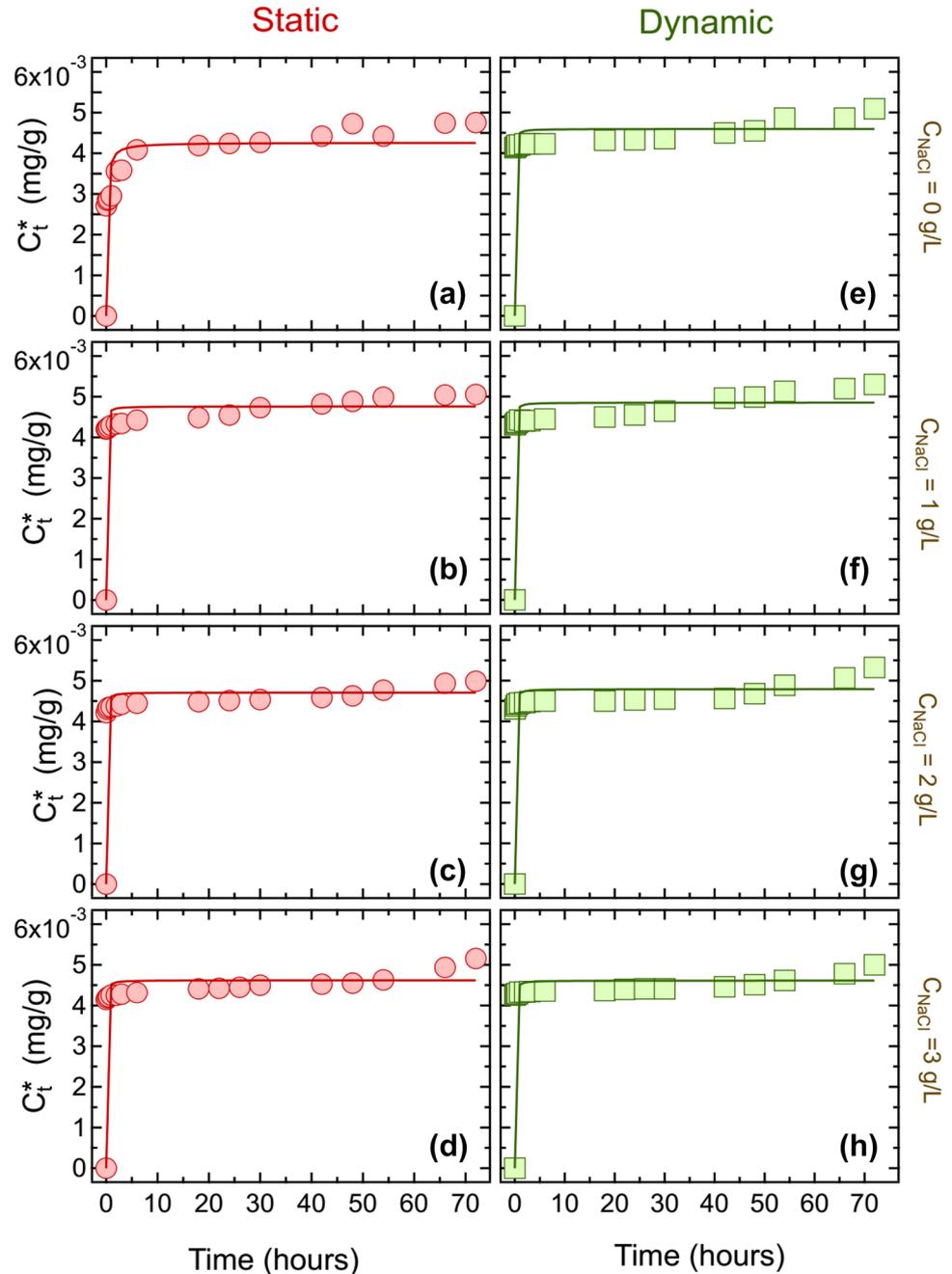
$$M_r = \frac{m_0}{M_{in}/U}, \tag{9}$$

where m_0 [$t \cdot M_{FA}/L^3$] is the total mass of the concentration breakthrough curve, and M_{in} [M_{FA}/L^2] is the mass injected over the void portion of the cross-sectional area of the column. The various model parameters have been estimated by fitting the analytical solution to the experimental data with the nonlinear least squares regression software ColloidFit (Katzourakis and Chrysikopoulos 2017).

Results and discussion

The data from the kinetic batch experiments of FA sorption onto quartz sand at 23 °C with three different initial FA concentrations ($C_{FA(0)} = 3, 5$ and 8 mg/L), under both static and dynamic conditions, are presented in Fig. 1. Furthermore, the effect of salinity on FA sorption onto quartz sand under static and dynamic conditions was investigated at 23 °C for three different NaCl concentrations (1, 2 and 3 g/L), and the experimental data are shown in Fig. 2. All kinetic experiments of FA sorption onto quartz sand were conducted over a time period of 7 days. All the kinetic FA sorption experimental data were fitted with a pseudo-second order sorption model (Eq. 3), using the autonomous multipurpose fitting software ColloidFit (Katzourakis and Chrysikopoulos 2017). The pseudo-second-order kinetic sorption model is used to describe physicochemical interactions such as chemisorption (Ho 2006; Wu et al. 2013), because FA sorption was assumed to involve a chemical reaction. The fitted model simulations were presented together with the experimental

Fig. 5 Effect of salinity on kinetic sorption of FA onto kaolinite particles under: **a–d** static conditions, and **e–h** dynamic conditions. Three different concentrations of NaCl were examined: **a, e** $C_{\text{NaCl}}=0$ g/L, **b, f** $C_{\text{NaCl}}=1$ g/L, **c, g** $C_{\text{NaCl}}=2$ g/L and **d, h** $C_{\text{NaCl}}=3$ g/L, at 23 °C

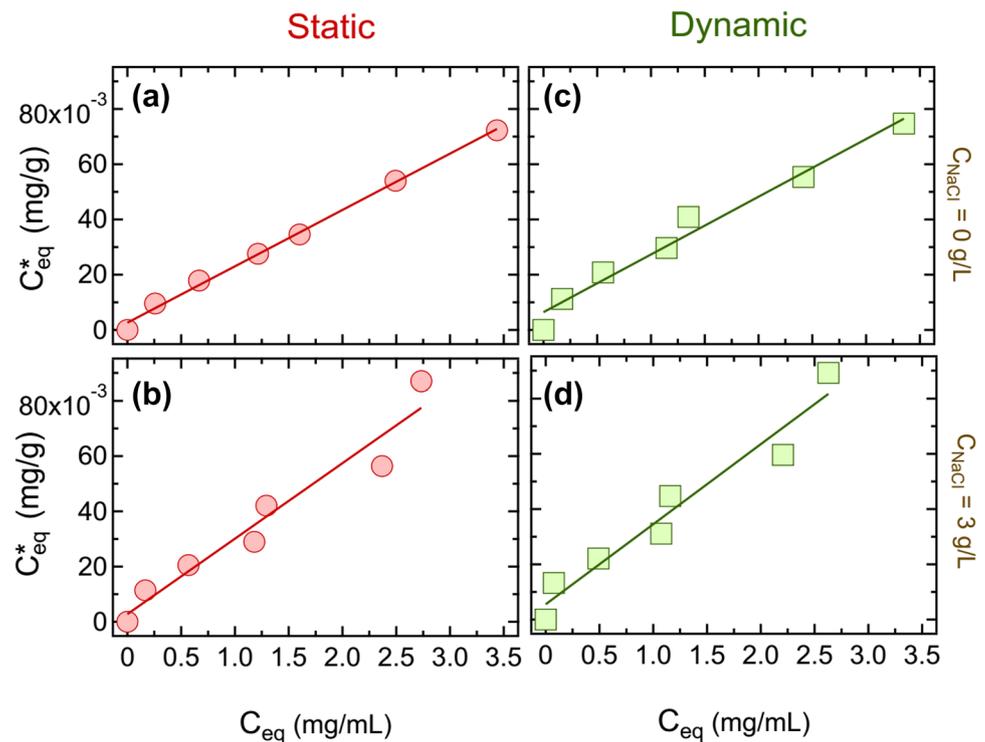


data (see Figs. 1, 2), and the corresponding fitted parameter values are listed in Table 1.

The kinetic sorption experimental data (see Figs. 1, 2) suggested that the amount of FA sorbed onto quartz sand progressively increased over the experimental duration of 7 days, which means that FA reached equilibrium relatively slowly. It should be noted that the time to reach equilibrium is controlled by several factors including solute concentration, adsorbent particle size, and degree of agitation (Moore et al. 1981). Similar trends were shown for all initial FA concentrations ($C_{\text{FA}(0)}$) examined. However, as expected,

the amount of FA mass sorbed onto quartz sand increased with increasing $C_{\text{FA}(0)}$. Furthermore, it was shown that the sorption rate of FA onto the quartz sand is slightly faster for dynamic conditions than static conditions for all three concentrations examined in this study, because agitation improves the contact of adsorbent solids with the liquid (Syngouna and Chrysikopoulos 2010). Furthermore, it is evident from Fig. 2 that the amount of FA sorbed onto quartz sand was slightly reduced with increasing salinity or equivalently increasing ionic strength. This is probably due to increased competition of positively charged FA species

Fig. 6 Equilibrium sorption data (isotherms) under static (a, b) and dynamic (c, d) conditions with $C_{\text{NaCl}} = 0$ g/L NaCl (a, b), and $C_{\text{NaCl}} = 3$ g/L NaCl (c, d). The solid lines are fitted lines with slope equal to K_d (R^2 in the range 0.90–0.99)



and electrolyte cations for sorption sites. This observation is consistent with other studies of sorption of organics onto soils (Laak et al. 2006).

The experimental data from the equilibrium sorption experiments of FA onto quartz sand under static and dynamic conditions with and without the presence of NaCl are presented in Fig. 3. The equilibrium sorption data were fitted with linear, Freundlich, and Langmuir isotherm models using ColloidFit (Katzourakis and Chrysikopoulos 2017). However, the data were best fitted with the linear isotherm (see Fig. 3). The fitted parameter values together with the corresponding coefficients of determination, R^2 , which ranged between 0.88 and 0.91, are listed in Table 2. Based on the K_d values of Table 2 it is evident that FA sorption is higher under dynamic than static conditions, and the presence of NaCl increased only very slightly the sorption of FA onto quartz sand.

The data from the kinetic batch experiments of FA sorption onto kaolinite ($\text{KG}_a\text{-1b}$) particles at 23 °C with three different initial FA concentrations ($C_{\text{FA}(0)} = 3, 5$ and 8 mg/L), under both static and dynamic conditions, are presented in Fig. 4, together with the fitted model simulations. Furthermore, the effect of salinity on FA ($C_{\text{FA}(0)} = 5$ mg/L) sorption onto $\text{KG}_a\text{-1b}$ particles under static and dynamic conditions was investigated at 23 °C for three different NaCl concentrations (1, 2 and 3 g/L), and the experimental data are shown in Fig. 5, together with the fitted model simulations. All fitted parameter values are listed in Table 1. The experimental duration of all experiments of FA sorption onto $\text{KG}_a\text{-1b}$ was

72 h (3 days). It was evident from the experimental data (see Figs. 4, 5) that the sorption of FA onto $\text{KG}_a\text{-1b}$ particles was a very fast process. A rapid increase in sorption of FA onto $\text{KG}_a\text{-1b}$ was observed within a few minutes. This fast sorption equilibrium is in agreement with previous studies (Yang et al. 2016; Salman et al. 2012). As for the experiments of FA sorption onto quartz sand, the amounts of FA sorbed onto $\text{KG}_a\text{-1b}$ increased with increasing $C_{\text{FA}(0)}$ (see Fig. 4). However, it was shown that salinity had a very minor effect on FA sorption onto $\text{KG}_a\text{-1b}$ (see Fig. 5). The amount of FA mass sorbed onto $\text{KG}_a\text{-1b}$ was practically the same for all C_{NaCl} concentrations used.

The experimental data from the equilibrium sorption experiments of FA onto $\text{KG}_a\text{-1b}$ under static and dynamic conditions with and without the presence of NaCl were presented in Fig. 6, together with the fitted linear isotherm model. The linear isotherm provided better fits than the Freundlich and Langmuir models. The fitted parameter values are listed in Table 2. It should be noted that the K_d values for FA sorption onto $\text{KG}_a\text{-1b}$ were much greater than the K_d values for FA sorption onto quartz sand (see Table 2), suggesting that kaolinite is a good sorbent for FA removal from aqueous solutions. Based on the K_d values of Table 2, it is evident that FA sorption is higher under dynamic than static conditions, and the presence of NaCl increased considerably the sorption of FA onto $\text{KG}_a\text{-1b}$. Similar results have been reported in the literature (Salman et al. 2012; Yang et al. 2016), suggesting that the sorption capacity of FA onto kaolinite can be used as a non-hazardous formaldehyde remover

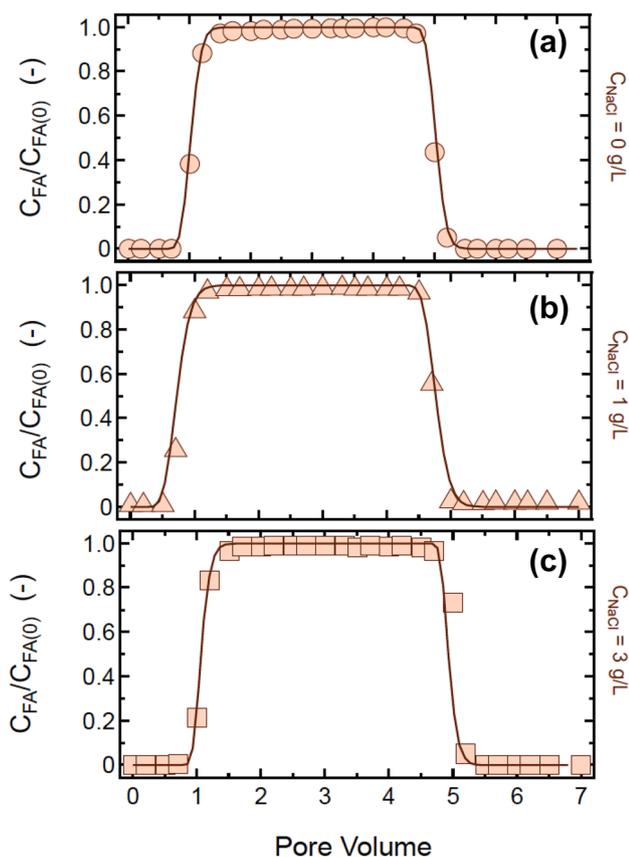


Fig. 7 Breakthrough data (symbols) and fitted model simulations (curves) for the transport of FA in a column packed with quartz sand with the addition of various NaCl concentrations: **a** $C_{\text{NaCl}}=0$ g/L, **b** $C_{\text{NaCl}}=1$ g/L, and **c** $C_{\text{NaCl}}=3$ g/L

from wastewaters and industrial effluents to avoid potential adverse effects to aquifers and human health.

The breakthrough data from FA flow-through experiments are presented in Fig. 7, together with the fitted transport model predictions. The breakthrough curves were plotted in the form of normalized concentrations (C/C_0) as a function of exchanged pore volumes. The parameters D , r_f , and r_r were estimated by fitting the analytical solution to the experimental FA breakthrough concentrations using the values of ρ_b , θ and U and the fitted D values are listed in Table 3. As it is shown in Fig. 7, the FA concentration decreased quickly to zero when the columns flushed with ddH₂O. Additionally, the normalized effluent

FA concentrations for all three different salt concentrations (0, 1, 3 g/L NaCl) were stabilized at approximately $C_{\text{FA}}/C_{\text{FA}(0)}=1.0$, suggesting that there was practically no FA retention by the quartz sand. The FA retained by the packed column, for each of the transport experiment, was estimated with ColloidFit (Katzourakis and Chrysikopoulos 2017), and the corresponding mass recoveries are listed in Table 3. This result is in agreement with the results from the batch experiments of FA sorption onto quartz sand conducted in this study. Therefore, FA can be considered as relatively mobile in water-saturated sandy soil column systems, at least under the experimental conditions of this study. Worthy of note is that very little FA retention occurred by the cleaned (acid washed) quartz sand. Possibly, the surfaces of sand grains in (oxic) sediments, which commonly contain coatings of oxides and clay minerals, may lead to greater FA retention than measured in this study.

Conclusions

The experimental results of this study suggested that FA was weakly sorbed onto quartz sand, whereas it was more significantly sorbed onto kaolin particles. The experimental data suggested that the sorption process involved a chemical reaction (chemisorption). More FA was sorbed onto the quartz sand and kaolinite particles under dynamic conditions than static conditions. Salinity (presence of NaCl) had minimum effect on FA sorption onto quartz sand, but somewhat more significant effect on FA sorption onto kaolinite (KG_a-1b). The equilibrium sorption of FA onto quartz sand and kaolinite, with and without the presence of NaCl, was adequately described by a linear isotherm. The migration of FA in water-saturated columns packed quartz sand was shown to be unaffected by salinity. Therefore, FA could be relatively mobile in natural soil and sediments, and could potentially pollute the aquatic environment with possible undesirable effects on living organisms and human health. Certainly, FA interaction with quartz sand would have been somewhat different if the sand was not cleaned. Our findings suggested that kaolinite could be a promising sorbent material for removal of FA from aqueous solutions and industrial effluents.

Table 3 Parameters for FA transport experiments ($Q=1$ mL/min)

NaCl (g/L)	ρ_b (g/cm ³)	θ (-)	U (cm/min)	D (cm ² /min)	r_f (1/min)	r_r (1/min)	M_r (%)
0	1.79	0.37	0.54	0.128	0.0126	0.853	97.5
1	1.79	0.37	0.54	0.234	0.0718	0.818	97.9
3	1.78	0.39	0.53	0.162	0.0815	0.826	100

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