Adsorption behavior of diclofenac-containing wastewater on three kinds of sewage sludge
Jingna Yan, Xiaohan Zhang, Wenting Lin, Chen Yang and Yuan Ren

ABSTRACT

Diclofenac (DCF) is one of the most frequently detected non-steroidal anti-inflammatory drugs (NSAIDs) in the water environment. One of the main removal routes of DCF in wastewater is sludge adsorption, and the mechanisms need to be investigated. In this study, the effects of adsorption time, temperature, pH value, and ionic strength on the adsorption of DCF on suspended particles (SP), secondary sedimentation tank sludge (SSTS) and concentrated sludge (CS) were investigated. The results showed that most of the adsorption of DCF by the three matrices was conducted in the first 4 h and equilibrium was achieved at 8 h. The adsorption kinetics were well fitted with the pseudo-second-order model and the rate constants were 0.29–0.88 mg·(µg·min)-¹, with chemical adsorption as the dominant one. Adsorption isotherm conformed to Freundlich, Langmuir and Linear adsorption isotherm models. The order of adsorption capacity was: CS > SSTS > SP, which was proportional to the organic matter content and specific surface area of the adsorbents. The decrease of the pH value and the increase of ionic strength promoted the adsorption of DCF. The results can provide data support for the removal of DCF from different treatment unit types in wastewater treatment plants.

Key words | adsorption behavior, diclofenac, sludge

INTRODUCTION

As a new type of pollutant, pharmaceuticals and personal care products (PPCPs) have attracted the attention of researchers due to the widespread pollution in ecological environment. NSAIDs are non-steroidal anti-inflammatory drugs that have analgesic, antipyretic, anticoagulant and anti-inflammatory effects. Diclofenac (DCF), one of the widely used NSAIDs, has the average consumption of 0.33 ± 0.29 g/person/year (Acuña et al. 2015). The industrial production and excretion by patients lead to the frequent detection of DCF in the influent and effluent of wastewater treatment plants (Kosma et al. 2014), surface water (Wang et al. 2010), underground water (Rabiet et al. 2006) and even drinking water (Rigobello et al. 2013), with a concentration level of 13 ng·L⁻¹–7.1 µg·L⁻¹. Some eco-toxicological studies demonstrated that trace levels of DCF could be accumulated in aquatic organisms and are toxic to microorganisms (Ferrari et al. 2005), algae (Ferrari et al. 2004), and fish (Schwaiger et al. 2004).

Up to now, biodegradation, physical and advanced oxidation technology are usually utilized in the removal of DCF. For high concentrations of DCF, advanced oxidation methods are easy to implement and efficient. Souza et al. reported the complete degradation of DCF by solar photo-Fenton oxidation in 90 min with 63% mineralization rate when the initial concentration of DCF was 20 mg L⁻¹ (Souza et al. 2014). Justo et al. compared the effects of ozone and UV/H₂O₂ oxidation, and found that DCF removal by low dosage of ozone was very low while UV/H₂O₂ could degrade DCF efficiently with high consumption of H₂O₂ (Justo et al. 2013). Chlorination oxidation is often applied to degrade DCF as well (Soufan et al. 2012). Adsorption and biodegradation are the main methods of DCF transformation in wastewater treatment plants (WWTPs). The effect of biodegradation of NSAIDs is related to the hydraulic retention time (Nikolaou et al. 2007), sludge age (Matsuo et al. 2011), and pH value (Tauxe-Wuersch et al. 2005), etc. Due to the -Cl and N-H functional groups contained in the molecular structure of DCF, the microbial activity is inhibited and the biodegradation rate does not exceed 10% (Nikolaou et al. 2007). It was
reported that the removal rate of DCF in the effluent of WWTP could reach 90–95% when combining a sequencing batch reactor and activated carbon adsorption (Reungoat et al. 2011). The DCF content in the sludge was 50 μg·kg⁻¹ to 450 μg·kg⁻¹ (Verlicchi et al. 2012). Although some researches have reported the adsorption in natural sediments (Jia et al. 2012), there are still many problems, such as the adsorption mechanisms, partition coefficient, and adsorption behavior of DCF that need to be solved.

In this study, suspended particles (SP), secondary sedimentation tank sludge (SSTS) and concentrated sludge (CS) from a sewage treatment plant were selected as the adsorption media. The adsorption kinetics, adsorption thermodynamics, and environmental factors of DCF on three media were studied. The study is expected to establish the relationship between sludge property and adsorption characteristics, provide a theoretical basis and technical parameters for the removal of DCF from sludge of different treatment units in WWTPs, so as to maximize the removal rate, reduce the total amount discharged into ecological environment, and minimize the ecological risk.

**MATERIALS AND METHODS**

**Sludges**

The three adsorption matrices were collected from Lijiao municipal treatment plant in Guangzhou city. SP were SS in the influent, SSTS were sludge flow out from biological tank, and CS were sludge treated by gravity concentration before dehydration. The three matrices were centrifuged for 5 mins at 3,500 rpm. After washing with tap water, suction filtration was performed. The sludge samples were air dried, ground, sieved through a 150 μm sieve, homogenized, and then stored in sealed containers at −20 °C before using. Excessive potassium dichromate-sulfuric acid method and specific surface area meters were used to determine the organic content and specific surface area of the three matrices. The results are shown in Table 1.

**Table 1** | Organic matrix content and specific surface area of the three matrices

<table>
<thead>
<tr>
<th>Different types of absorbents</th>
<th>Organic content (g·kg⁻¹)</th>
<th>Specific surface area (m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended particles (SP)</td>
<td>145.3</td>
<td>0.3952</td>
</tr>
<tr>
<td>Secondary sedimentation tank sludge (SSTS)</td>
<td>312.4</td>
<td>0.6542</td>
</tr>
<tr>
<td>Concentrated sludge (CS)</td>
<td>581.1</td>
<td>0.8953</td>
</tr>
</tbody>
</table>

**Chemicals**

DCF (CAS#15307-86-5, C₁₄H₁₁Cl₂NO₂, >99.9%, pKa = 4.15) was purchased from Augsburg (Germany). Methanol, glacial acetic acid (CH₃COOH, 98%), sodium citrate (Na₃C₆H₅O₇·2H₂O, 98%), urea (CO(NH₂)₂, 98%), sodium hydroxide (NaOH, 98%), sodium chloride (NaCl, 98%), and calcium chloride (CaCl₂, 98%) were purchased from ANPEL Laboratory Technologies Inc. (Shanghai, China).

Hydrochloric acid (HCl, 32%) was purchased from Aladin Industria Inc. (Shanghai, China).

Stock solution for DCF (1,000 mg L⁻¹) was prepared with methanol as the solvent. Buffer solutions for pH 2.0, 7.0 and 12 were prepared as background solution using an electrolyte solution including 10 mM CaCl₂, 5 mM NaOH and 5 mM HCl before each sorption experiment. The ratio of methanol:water was lower than 0.2% (v/v) to prevent solvent effect for sorption.

**DCF sorption onto sludge**

The effects of adsorption time, pH value of the solution, temperature, ionic strength and dissolved organic matter on the adsorption behavior of DCF on the three matrices were investigated with batch experiments. The experiment was conducted with sludge but without DCF, and with DCF alone (no sludge) as controls.

DCF sorption experiments were conducted at 30 °C in 250 mL Erlenmeyer flasks. Two grams of the three matrices each were placed into the flasks, and then electrolyte solutions were carefully added into the flasks to prepared 5 mg L⁻¹ DCF solution with pH = 7. The flasks were placed in a shaker and shaken at 150 rpm for 24 h. The samples were collected periodically. The sample mixtures were centrifuged at 10,000 rpm for 5 min and supernatant was decanted from the centrifugation. Then, the supernatant was filtered through a 0.45 μm water filtration membrane (Polyethersulfone, PES) and 1.0 mL of supernatant was taken for HPLC analysis. At any time t, the adsorption of DCF can be calculated by Equation (1):

\[ Q_t = \frac{(c_0 - c_t) \times V \times 1000}{m} \]  

where \( Q_t \) is the adsorption capacity of DCF (μg·g⁻¹); \( c_0 \) is the initial concentration of DCF (mg·L⁻¹); \( c_t \) is the concentration of DCF at t time; \( V \) is the volume of solution (L); \( m \) is the weight of sludge used (g).
Adsorption kinetics and DCF diffusion mechanisms in the sludge

The obtained data were used to calculate the kinetics parameters. The partition coefficient $K_d$ (L·kg$^{-1}$) can be calculated by Equation (2):

$$K_d = \frac{C_s}{C_e} = \frac{(C_0 - C_e)}{V \times 1000 \times m_{ce}}$$

where $C_s$ and $C_e$ are the concentrations of DCF (mg·L$^{-1}$) in the solid phase and liquid phase when adsorption equilibrium was achieved, respectively. $C_0$ is the initial concentration of DCF in the solution, and $m$ is the weight of sludge used (g).

Pseudo-first-order kinetics Equation (3) (Andradakis 1995) and pseudo-second-order kinetics Equation (4) (Ho & McKay 1999) were applied to fitting the adsorption data of DCF in three kinds of matrices.

$$\ln \left( \frac{Q_e}{Q_t} \right) = \ln Q_e - k_1t$$

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e} + \frac{t}{Q_e}$$

where $t$ is the adsorption time (min); $Q_e$ and $Q_t$ are the amounts of adsorption of DCF (μg·g$^{-1}$) by the three matrices at equilibrium and at time $t$; $k_1$ (min$^{-1}$) and $k_2$ (g·μg$^{-1}$·min$^{-1}$) are the rate constants for the pseudo-first-order and pseudo-second-order kinetic equations, respectively.

To understand the adsorption mechanisms, the diffusion rate constants of liquid film diffusion, particle diffusion, and adsorption reaction were calculated with Equations (5)–(7) and the slowest step among them is the speed limit step (Lin & Hsieh 1996).

$$-\ln \left( 1 - \frac{Q_t}{Q_e} \right) = K_a t$$

$$1 - 3 \left( 1 - \frac{Q_t}{Q_e} \right)^{\frac{3}{2}} + 2 \left( 1 - \frac{Q_t}{Q_e} \right) = K_b t$$

$$1 - \left( 1 - \frac{Q_t}{Q_e} \right)^{\frac{1}{3}} = K_c t$$

where $K_a$, $K_b$, and $K_c$ are the rate constants for liquid film diffusion, particle diffusion, and adsorption reactions, respectively.

Isothermal adsorption experiment

In this study, we selected three temperatures (25 °C, 30 °C and 35 °C) to investigate the effect of the sorption of DCF onto sludge based on the local outdoor temperature. The initial concentrations of DCF were set to 0.5, 1.0, 2.0, 3.0, and 5.0 mg·L$^{-1}$.

The isothermal adsorption process can be described by Langmuir (Equation (8)), Freundlich (Equation (9)) and Linear models (Equation (10)) (Ho & McKay 2004; Andersen et al. 2005; Inbaraj et al. 2006).

$$Q_e = \frac{Q_m K_L c_e}{1 + K_L c_e}$$

$$Q_e = K_F c_e^{1/n}$$

$$Q_e = K_N c_e + b$$

where $Q_m$ is the maximum single-layer adsorption capacity of sludge to DCF. $K_L$, $K_F$ and $K_N$ are the Langmuir adsorption coefficient, Freundlich adsorption coefficient, and Linear adsorption equilibrium coefficient. The Langmuir adsorption model is a monolayer adsorption model. The larger the adsorption constant $K_L$, the more substances were adsorbed. The Freundlich model is an empirical model that mainly describes the adsorption equilibrium of a multiphase adsorption surface. $K_N$ indicates the strength of adsorption, and $K_N$ and $b$ are constants.

Gibbs free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) were calculated through Equations (11)–(13).

$$\Delta G^0 = -RT \ln K_d$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where $R$ is the ideal gas molar constant, 8.314; $K_d$ is the solid-liquid partition coefficient; and $T$ (K) is absolute temperature.

Effect of environmental factors on adsorption

Five pH conditions (3.0, 5.0, 7.0, 9.0 and 11.0) were selected to investigate the differences in the sorption of DCF with neutral, neutral/anionic, and anionic species onto sludge. To estimate the ionic strengths effect on DCF sorption, the sorption experiments were conducted at 0, 20, 40, 60,
80 and 100 mmol L\(^{-1}\) NaCl solution. Citrate and urea were selected as the representative dissolved organic matter to investigate the effects on the adsorption and their concentrations were 0, 0.01, 0.1, and 1.0 mmol L\(^{-1}\), respectively.

**Analytical methods**

The concentration of DCF in aqueous solution was measured by high performance liquid chromatography (HPLC) equipped with the Agilent Eclipse XDB column (4.6 mm \(\times\) 150 mm, 5 \(\mu\)m). The mobile phase of this analysis was a mixture of 25% deionized water (containing 1\% CH\(_3\)COOH) and 75\% methanol. DCF was measured at a flow rate of 1.0 mL min\(^{-1}\) at 276 nm. The limit of detection of DCF is 0.01 mg L\(^{-1}\).

**Quality assurance and quality control**

All the experiments were set up in triplicate and the mean values were used to evaluate the results. Quality assurance and quality control (QA/QC) was implemented to ensure the accurate quantification of DCF. The analyses in blank samples were below LOD. Accuracy was 12.8\% for DCF and precision was 0.071.

**Data/statistical analysis**

The correlation between equilibrium adsorption, organic content and specific surface area was analyzed by SPSS 20.0. The Pearson correlation coefficient (r, two tailed) was used to analyze the linear correlation among the three. \(r > 0\) indicated a positive correlation between variables; \(r < 0\) indicated a negative correlation between variables.

**RESULTS AND DISCUSSION**

The pre-experimental results showed that the effects of the bottle wall and other losses could be ignored in the experiment.

**Adsorption kinetics**

The DCF adsorption performances of three matrices were tested and the results are shown in Figure 1. The adsorption behaviors of the three matrices for DCF were very similar. At the beginning of the adsorption, obvious adsorption occurred within 0–4 h by all of the adsorbents. As the adsorption time increased, the adsorption amount slightly increased and the adsorption time was extended to 8 h to achieve equilibrium. K\(_d\) for SP, SSTS, and CS were 18.22, 58.43, and 84.55 L kg\(^{-1}\), respectively. Carballa et al. (2007) reported a K\(_d\) for sludge digestion of 65.5 ± 23.1 L kg\(^{-1}\), which was similar to the result of SSTS in this study.

Figure 2 shows the effect of initial concentrations of DCF on the adsorption. When the adsorption sites on the sludge were not saturated, the adsorption capacity increased with the increase in initial DCF concentration. The equilibrium adsorption amount for CS is larger than that of SSTS and SP. This result verified that the adsorption capacity is positively correlated with organic matter content (\(r = 0.905\)) and specific surface area (\(r = 0.959\)); that is, CS > SSTS > SP, which supports the conclusion of
Muter (Muter et al. 2017). The correlation coefficient of $Q_e \sim$ organic content and $Q_e \sim$ specific surface area was 0.902 and 0.959, respectively, which indicated that the specific surface area has a greater influence on the amount of adsorption than that of the organic content.

**Kinetics models**

Adsorption kinetics can reflect the rate of adsorption, adsorption characteristics and influencing factors. According to Equations (2) and (3), the pseudo-first-order and pseudo-second-order kinetic model fitting curves are shown in Figure 3(a) and 3(b). The fitting parameters are shown in Table 2. To compare the adsorption kinetics precisely, the pseudo-second-order kinetic equation was adopted ($R^2 > 0.99$), indicating that the adsorption behavior was dominated by chemical adsorption. The ionic form of DCF can be ion-exchanged with hydroxyl or carboxyl groups on the sludge or connected in the form of conjugated electron pairs (Song 2014).

The fitting results of the adsorption speed limit steps for the three matrices-adsorbing DCFs are shown in Table 3. It can be seen that the adsorption rate constant followed the same order as $K_a < K_b < K_c$ which means the adsorption reaction was the rate-limiting step regardless of the type of matrix. Meanwhile, the adsorption rate constant followed the order of $CS > SSTS > SP$ during liquid film diffusion, particle diffusion, and adsorption reaction processes.

### Table 2 | Kinetic parameters for the adsorption of DCF onto three matrices

<table>
<thead>
<tr>
<th>Different types of sludge</th>
<th>$Q_{e,exp}$ (μg·g$^{-1}$)</th>
<th>$Q_{e,cal}$ (μg·g$^{-1}$)</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>$Q_{e,cal}$ (μg·g$^{-1}$)</th>
<th>$k_1 g \cdot (μg \cdot min)^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP</td>
<td>61.89</td>
<td>25.03</td>
<td>0.0094</td>
<td>0.9694</td>
<td>64.61</td>
<td>0.00088</td>
<td>0.9981</td>
</tr>
<tr>
<td>SSTS</td>
<td>104.39</td>
<td>78.55</td>
<td>0.0115</td>
<td>0.9603</td>
<td>112.48</td>
<td>0.00029</td>
<td>0.9946</td>
</tr>
<tr>
<td>CS</td>
<td>117.21</td>
<td>69.88</td>
<td>0.0110</td>
<td>0.9831</td>
<td>123.96</td>
<td>0.00033</td>
<td>0.9981</td>
</tr>
</tbody>
</table>

* $Q_{e,exp}$ is the equilibrium adsorption amount obtained from the experiment, $Q_{e,cal}$ is the equilibrium adsorption amount calculated.

### Table 3 | The speed limit steps for the adsorption of DCF onto three matrices

<table>
<thead>
<tr>
<th>Different types of sludge</th>
<th>Liquid film diffusion</th>
<th>Particle diffusion</th>
<th>Adsorption reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_e$/min$^{-1}$</td>
<td>$R^2$</td>
<td>$K_e$/min$^{-1}$</td>
</tr>
<tr>
<td>SP</td>
<td>0.0093</td>
<td>0.9652</td>
<td>0.0016</td>
</tr>
<tr>
<td>SSTS</td>
<td>0.0095</td>
<td>0.9750</td>
<td>0.0018</td>
</tr>
<tr>
<td>CS</td>
<td>0.0110</td>
<td>0.9811</td>
<td>0.0019</td>
</tr>
</tbody>
</table>
From the above analysis, it can be seen that the three matrices have similar adsorption characteristics for DCF. The adsorption isotherm was obtained using the 8 h adsorption equilibrium time. The isothermal adsorption curves of DCF for SP, SSTS and CS at different temperatures are shown in Figure 4. Corresponding relevant parameters are listed in Table 4. The results showed that the three models of Langmuir, Freundlich and Linear could better

Table 4 | Adsorption isotherms fitting parameters for DCF onto three matrices

<table>
<thead>
<tr>
<th>Different types of sludge</th>
<th>T (°C)</th>
<th>Langmuir</th>
<th></th>
<th>Freundlich</th>
<th></th>
<th>Linear</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Qm (mg g⁻¹)</td>
<td>Kd</td>
<td>R²</td>
<td>Kf</td>
</tr>
<tr>
<td>SP</td>
<td>25</td>
<td>9.155</td>
<td>0.0018</td>
<td>0.9963</td>
<td>0.0166</td>
<td>1.001</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3933</td>
<td>0.0034</td>
<td>0.9959</td>
<td>0.0117</td>
<td>1.129</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.0956</td>
<td>0.0072</td>
<td>0.9663</td>
<td>0.0084</td>
<td>1.148</td>
</tr>
<tr>
<td>SSTS</td>
<td>25</td>
<td>13.62</td>
<td>0.0012</td>
<td>0.9841</td>
<td>0.0503</td>
<td>0.9766</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2.253</td>
<td>0.0034</td>
<td>0.9936</td>
<td>0.0381</td>
<td>0.9808</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.1624</td>
<td>0.0072</td>
<td>0.9881</td>
<td>0.0161</td>
<td>1.042</td>
</tr>
<tr>
<td>CS</td>
<td>25</td>
<td>28.99</td>
<td>0.0383</td>
<td>0.9898</td>
<td>0.0844</td>
<td>1.017</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>9.788</td>
<td>0.0014</td>
<td>0.9901</td>
<td>0.0412</td>
<td>1.117</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>2.294</td>
<td>0.0023</td>
<td>0.9723</td>
<td>0.0220</td>
<td>0.9803</td>
</tr>
</tbody>
</table>
fit the adsorption behaviors of three kinds of matrices to DCF (0.9802 ≤ R² ≤ 0.9991), which showed that the adsorption mechanisms of DCF by three kinds of matrices are monolayer adsorption and distribution effect.

**Adsorption thermodynamics**

From Figure 4 and Table 4, it could be concluded that Qₘ, Kₑ, and Kₙ of SP, SSTS, and CS decreased as the temperature increased, which indicated that the adsorption was an exothermic reaction. The increase of temperature can accelerate the release of organic compounds in the absorbent and improve the solubility of organic compounds, which leads to a decrease of the absorption amount. Table 5 demonstrates ΔG₀, ΔH₀, and ΔS₀ under different temperatures, and we can find that the ΔG₀ of DCF adsorption by the three matrices is negative, which indicate that the adsorption is a spontaneous and exothermic reaction. ΔS₀ is a negative value, indicating that the entire system tends to be ordered after the adsorption reaction.

**Effect of pH on DCF sorption**

The pH of the solution can change the form of the DCF (shown in Figure 5) as well as the surface charge and chemical properties of the adsorbent to affect the adsorption kinetics and equilibrium properties. The effect of pH on the adsorption of DCF by the three matrices is shown in Figure 6. It can be seen that the effect of pH on the adsorption of DCF on SP, SSTS, and CS was similar. When the pH of the solution ranged from 3 to 7, the adsorption of DCF decreased but the trend was slow. When the pH was in the range of 7–11, the adsorption amount decreased rapidly. The molecular structure of DCF contains -COOH, which can exist in the form of ionic DCF⁻ and molecular DCF.

Table 5 | Thermodynamic parameters for adsorption of DCF onto three matrices

<table>
<thead>
<tr>
<th>Sludges</th>
<th>T/K</th>
<th>ΔG₀/(kJ·mol⁻¹)</th>
<th>ΔH₀/(kJ·mol⁻¹)</th>
<th>ΔS₀/(J·(mol·K)⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP</td>
<td>298</td>
<td>−9.926</td>
<td>−55.37</td>
<td>−218.8</td>
<td>0.9754</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>−10.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>−12.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSTS</td>
<td>298</td>
<td>−7.292</td>
<td>−87.21</td>
<td>−316.9</td>
<td>0.9980</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>−8.767</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>−10.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS</td>
<td>298</td>
<td>−6.093</td>
<td>−103.1</td>
<td>−365.8</td>
<td>0.9747</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>−7.453</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>−9.762</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bui & Choi (Bui & Choi 2009) reported that when pH < pKₐ, the acidic drug was a neutral molecule and the non-electrostatic interaction through the hydrogen bond was adsorbed on the silica surface. In this study, when pH was 3.0–4.15, neutral DCF molecules were adsorbed by non-electrostatic interaction with the sludge surface. When pH 4.15–7, DCF coexisted in the anionic form and the molecular form, and the surface electronegativity of the sludge increased. Then the anionic form of DCF repelled the sludge, and the adsorption amount slowly decreased. At pH > 7, the DCF was in the anionic form (hydrophilic) and hardly adsorbed onto the substrate because the sludge was negatively charged and electrostatically repelled each other. This showed that the adsorption of DCF is affected by its hydrophobicity (neutral form), and the amount of adsorption decreases with the increase of pH value.
Effect of ionic strength on DCF sorption

The ionic strength indirectly influences the adsorption behavior of DCF in three matrices by directly affecting the solubility of DCF and the adsorption capacity of adsorbents. The effect of ionic strength on the adsorption of DCF on the three matrices is shown in Figure 7. When the ionic strength increased from 0 to 100 mmol L$^{-1}$, the amount of DCF adsorbed by SP, SSTS, and CS increased from 0.0656 mg g$^{-1}$ to 0.1145 mg g$^{-1}$, 0.1041 mg g$^{-1}$ to 0.1523 mg g$^{-1}$, and 0.1167 mg g$^{-1}$ to 0.1787 mg g$^{-1}$, respectively. This indicated that the adsorption amount increased as the ionic strength increased.

On one hand, the presence of Na$^+$ led to salting out of the DCF and the solubility of the DCF decreased. The amount of DCF adsorbed through the partitioning of organic carbon increased and the salting-out action inhibited the release of organic carbon in the sludge to the solution. The distribution of organic carbon in the sludge enhanced the adsorption capacity of the matrix (Wu et al. 2010). On the other hand, the increasing Na$^+$ concentration can neutralize the negative charge on the substrate surface, reduce the electrostatic repulsion between the surface negative charge and the DCF$^-$, and promote DCF$^-$ adsorption onto the substrate surface through electrostatic attraction. This adsorption mechanism can also be referred to as bridging adsorption; that is, the -COOH of DCF forms a bridging effect between Na$^+$ and the matrix (Burns et al. 2006; Oh et al. 2013, 2016).

Effect of DOM on DCF sorption

Citrate and urea are representative of DOM and have high solubility in water. The effect of citric acid and urea on the adsorption of DCF by three matrices is shown in Figure 8. The addition of citrate decreased the DCF adsorption by about 50% in the three matrices with no obvious change for urea. This may be because citrate has three carboxyl groups and can form a citrate-DCF complex, which leads to a decrease in the amount of adsorption. Urea does not change the properties of organic matter and the sediment surface, and there is no interaction with DCF and sludge. Therefore, urea has no effect on the adsorption of DCF by three kinds of sludge.

CONCLUSION

(1) The adsorption process of DCF by suspended particulate matter, SSTS and CS are similar and the adsorption
equilibrium time was 8 h. The adsorption capacity was positively correlated with the organic content and specific surface area of the matrix.

(2) The adsorption behaviors of DCF by the three kinds of matrices are fitted to the pseudo-second-order kinetic equation. Chemical adsorption dominated the adsorption behavior and the adsorption reaction was the rate-limiting step of the entire adsorption behavior.

(3) The result of adsorption thermodynamics showed that the three models of Langmuir, Freundlich and Linear fit the adsorption isotherms of DCF on three matrices well and the adsorption reaction is an exothermic reaction.

(4) The pH value significantly affected the adsorption of DCF, and the amount of adsorption decreased with increasing pH. The increase of ionic strength promoted the adsorption of DCF by the three matrices. Dissolved organic citrate reduced the adsorption of DCF but urea had no effect on the adsorption of DCF.

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