Adsorption of diclofenac onto goethite: Adsorption kinetics and effects of pH

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Highlights

- The increasing pH decreased the adsorption of diclofenac (DCF) to goethite.
- DCF adsorption to goethite was well fitted with Pseudo-second-order model.
- The carboxyl group (–COOH) might be involved in the adsorption.
- DCF and goethite formed bidentate chelate and bridging bidentate complexes.

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Abstract

The adsorption of diclofenac (DCF), one of the widely used non-steroidal anti-inflammatory drugs, onto the surface of goethite was investigated with batch experiments. The adsorption at different pH values (5.3, 7.4, and 10.0) were well fitted with the pseudo-second-order model. The results showed that the adsorption of DCF onto goethite was strongly dependent on solution pH. The amount of adsorbed DCF decreased with increasing pH due to electrostatic repulsive interactions. Fourier transform infrared (FTIR) results indicated that carboxyl group (–COOH) might be involved in the adsorption, and DCF formed bidentate chelate and bridging bidentate complexes on the surface of goethite.

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1. Introduction

Diclofenac (2-[2,6-dichlorophenyl] amino) phenyl acetic acid, DCF), a common non-steroidal anti-inflammatory, is always used for the treatment of painful and inflammatory conditions for human and animals. The global consumption of DCF is estimated on an annual basis to be about 940 tons (Zhang et al., 2008). DCF has been detected in groundwaters and surface waters in different areas, such as Germany (Ternes, 1998), Pakistan (Scheurell et al., 2009), Spain (Lopez-Serna et al., 2013), Europe (Loos et al., 2010), China (Wang et al., 2010; Zhao et al., 2010), and the concentrations of DCF detected range from not detected to 4400 ng L⁻¹ (Ternes, 1998; Heberer, 2002; Scheurell et al., 2009; Loos et al., 2010; Wang et al., 2010; Zhao et al., 2010; Lopez-Serna et al., 2013). It is also one of the few pharmaceutical and personal care products (PPCPs) which could be detected in the drinking water (Vulliet and Cren-Olive, 2011). The presence of DCF and its metabolites in environment has adverse effects on organisms (Oaks et al., 2004; Schmitt-Jansen et al., 2007).

Adsorption of PPCPs to soils/sediments is a major process affecting their mobility and ultimate fate in the environment (Scheyt et al., 2004; Yu and Bi, 2015). Previous studies showed that DCF was retarded (Retardation factor = 2.0) in the soil column.
(medium grained sand, 95.3%), whereas no significant degradation was observed under the prevailing conditions (Scheytt et al., 2004). Soil organic matter (SOM) was a key factor controlling the migration of DCF in two soils (Revitt et al., 2014), and adsorption of DCF to sediments was also evidently affected by the content of SOM (floc) of soils and sediments (Chefetz et al., 2008; Revitt et al., 2014; Styszko, 2015).

In fact, the interactions between PPCPs and soils/minerals were very complex and included several mechanisms, such as cation bridging (Wu et al., 2012), cation exchange (Wang et al., 2011), hydrogen bonding (Sali et al., 2014) and surface complexation (Paul et al., 2014). Iron (hydr)oxides are important minerals in soils/sediments (Schwertmann and Latham, 1986; Schwertmann, 1988), which might influence the adsorption of DCF to soils/sediments. Goethite is an abundant and important hydrous iron oxide in soils, which is usually used as a model adsorbent to investigated the adsorption of PPCPs to iron-rich soil minerals (Lin et al., 2012; Zhao et al., 2011). However, the study on adsorption of DCF onto goethite was scarcely reported. In this study, the effects of reaction time and pH on the adsorption of DCF onto goethite were investigated.

2. Materials and methods

2.1. Materials

Goethite (chemical reagent grade) was obtained from Sigma-Aldrich (USA) and confirmed by X-ray diffraction (D8 ADVANCE, Bruker, Germany) measurement. The specific surface area of goethite was 18.3 m$^2$ g$^{-1}$, which was determined using the BET method (Micrometer, ASAP2020, USA). The intrinsic surface deprotonation constants (pK$_{a1}$ and pK$_{a2}$) of goethite were respectively 5.69 and 8.12 (Mamindy-Pajany et al., 2011), and the point of zero charge (PZC) of goethite was 6.9 (Mamindy-Pajany et al., 2011).

The target compound diclofenac sodium salt (>98%) was purchased from Sigma-Aldrich (USA). The chemical formula of diclofenac sodium is C$_{14}$H$_{10}$Cl$_2$NNaO$_2$, and the molecular weight is 318.14. The protonation constant (pK$_{a1}$) is 4.15 (Torrellas et al., 2015). At pH < 4.15, uncharged molecules were formed, and they were anionic by the deprotonation of carboxyl functional groups with the increasing pH. Methanol (HPLC grade) was purchased from Honeywell Burdick & Jackson (USA). All chemicals were purchased in analytical purity or higher and used without any further purification. All solutions were prepared using ultrapure water (MILLI-Q, USA).

2.2. Batch experiment

Stock solution of DCF (100 mg L$^{-1}$) was prepared by dissolving appropriate amount of diclofenac sodium salt in ultrapure water, and stored at 4 °C in the dark. The required DCF concentration was obtained by dilution of the stock solution.

Experiments at different pH (5.3, 7.4, and 10.0) were conducted at different reaction time. 0.4 g of goethite was weighed into 40 mL amber sampler vial, and 20 mL DCF solution (1 mg L$^{-1}$, l = 0.01 M NaCl) was added. The pH of suspensions was adjusted by adding 0.01 M HCl or 0.01 M NaOH. The samples were mixed in a reciprocal shaker at 175 rpm and 25 °C in the dark, and were then shaken for 5 min, 10 min, 20 min, 45 min, 67 min, 130 min, 240 min, 480 min, 720 min, 1440 min, and 2880 min. The supernatants (1 mL) were taken for analyzing the concentration of DCF. The final pH of each sample was measured using a pH meter (Sartorius PB-10, Germany).

The amounts of DCF adsorbed on goethite at time $t$ were calculated by the following equation:

$$q_t = \frac{V(C_0 - C_t)}{M}$$

where $q_t$ (µg g$^{-1}$) is the DCF concentration in soil-phase at time $t$; $C_0$ (mg L$^{-1}$) and $C_t$ (mg L$^{-1}$) are the DCF concentrations in aqueous-phase at initial time and time $t$; $V$ (L) is the volume of aqueous-phase; $M$ (g) is the mass of goethite.

In order to investigate the adsorption process, kinetic experiment data were analyzed by the pseudo-first-order kinetic model and pseudo-second-order kinetic model, respectively, which were shown as follows:

Pseudo first-order kinetic model (Ho and McKay, 1998):

$$q_t = q_e (1 - e^{-k_1 t})$$

Pseudo second-order kinetic model (Ho, 2006):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$

where $t$ (min) is the reaction time, $k_1$ (min$^{-1}$) and $k_2$ (g µg$^{-1}$ min$^{-1}$) represent the adsorption rate constants; $q_e$ and $q_t$ (µg g$^{-1}$) are the adsorbed amount of DCF by goethite at equilibrium and time $t$ (min), respectively.

Adsorption edges were also obtained from batch experiments. The initial concentrations of DCF were 250, 500, 1000, 1500, and 2000 µg L$^{-1}$. The final concentration of goethite was 20 g L$^{-1}$, and the background electrolyte was 0.01 M NaCl. Acid or base (0.01 M HCl or 0.01 M NaOH) was drop-wise added to adjust solution pH in the range of 5–11. The experiments were conducted similarly as detailed above, except that samples were conducted in the equilibrium time of 24 h. All experiments were conducted in triplicates. Meanwhile, blank samples (samples containing goethite but without DCF) and control samples (only containing DCF) were also carried out.

2.3. Chemical analysis

The concentration of DCF in solution was determined using a high performance liquid chromatography (HPLC) (LC-20AT, Shimadzu) with an Inertsil@ ODS-SP column (4.6 mm × 250 mm, 5 µm particle size). The mobile phase consisted of 75% methanol and 25% phosphate (0.025 M, pH 2.5). The flow rate is 1 mL min$^{-1}$. 10 µL of sample was injected using an auto-sampling device, with the detection wavelength set to 277 nm. The column temperature was kept at 35 °C. No significant interferences were found from blank and control samples.

2.4. Spectroscopic analysis

Samples for FTIR analysis were taken from three batch experiments, the initial DCF concentration was 2000 µg L$^{-1}$, and the final solution pH were 5.27, 7.13 and 9.21, respectively. At equilibrium time, solids were separated by centrifugation and dried at 45 °C for 48 h. Then the samples were diluted with KBr powder (sample: KBr = 1:50) and pressed pellets for testing. The infrared spectra of samples were recorded by a FTIR spectrometer (FTIR-650, Guangdong, Tianjin), operating in the wavenumber range of 400–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.
3. Results and discussion

3.1. Adsorption kinetics

The adsorption kinetics of DCF on goethite were shown in Fig. 1. Different behaviors were observed at different pH conditions. At pH 5.26, DCF was aggregated quickly onto the goethite surface. Similar phenomenon during the adsorption process of PPCPs (i.e. tetracycline and sulfamethazine) on goethite was also reported (Zhao et al., 2011; Guo et al., 2013). The sorption of DCF on goethite reached the apparent equilibrium at 480 min. The amount of adsorbed DCF was 23.53 µg g⁻¹ at 5 min, and then reached a constant level of 25.47 µg g⁻¹. The adsorption process at pH 9.96 was quite different from that at pH 5.26. At pH 9.96, the adsorption of DCF on goethite obtained apparent equilibrium in 1440 min and the adsorbed amount was 1.59 µg g⁻¹, which was much lower than that at pH 5.26.

When solution pH increased, the amount of DCF adsorbed to goethite decreased significantly (Fig. 1). In the pH range (pH 5–10) of this study, DCF was anionic (pH > pKᵢ). The surface of goethite was positive at pH < PZC of goethite (6.9), and was negative at pH > PZC. At pH 5.26, more DCF was adsorbed due to the electrostatic attraction between the negative charged DCF molecules and the positive charged goethite. At pH > 6.9, adsorption of DCF to goethite decreased with the increasing pH, because of the electrostatic repulsion between DCF molecules and the surface of goethite.

At pH 7.40, the equilibrium adsorbed amount of DCF was 9.33 µg g⁻¹. As shown in Fig. 1, the fluctuation of adsorbed amount of DCF with reaction time was relatively large. This had negatively correlation with solution pH (Fig. S1). However, the adsorbed amount of DCF had no significant correlation with system pH at pH 5.26 and pH 9.96 (Figs. S2 and S3). At pH 7.40, the solution pH was close to the point of zero charge (PZC) of goethite, and the net charge of goethite surface gradually changed into negative charge. The fluctuation in the amounts of DCF adsorbed to goethite was caused by the electrostatic interactions. We should notice that some DCF was still adsorbed to goethite at pH > PZC, so other mechanisms (i.e. surface complexation) might be also involved. And this result was reported in previous studies on the adsorption of other antibiotics containing carboxyl group (Trivedi and Vasudevan, 2007; Paul et al., 2014; Qin et al., 2014b).

The pseudo-first-order kinetic and pseudo-second-order kinetic models were used to simulate the experiment data (Table 1), and only the pseudo-second-order model could fit the adsorption kinetics well (R² > 0.96, P (prob > F) < 10⁻⁵). And qₑobs that obtained with the pseudo-second-order model were similar to qₑexp. The rate constants (k₂) at different pH conditions were 4.40 × 10⁻³, 1.40 × 10⁻², and 3.00 × 10⁻³ g µg⁻¹ min⁻¹ respectively. Obviously, the rate constant (k₂) was related to the solution pH since it decreased in the following pH order: 5.26 > 9.96 > 7.40. It was also reported that protons took part in the chemical complexation between functional groups on PPCPs and goethite (Paul et al., 2012).

Therefore, the low pH was more favorable for adsorption. The minimum kinetic rate constant (k₂) was observed at pH 7.40, which due to unstable charge of goethite surface at this condition.

3.2. Effect of pH

The adsorption edges of DCF to goethite were shown in Fig. 2. In order to investigate the adsorption behavior of DCF at both low and high concentration to goethite adequately, the initial concentrations of DCF ranged from 250 to 2000 µg L⁻¹. With increasing initial concentration of DCF, the adsorbed amount of DCF also increased at different pH. The initial concentrations of DCF ranged from 250 to 2000 µg L⁻¹, the adsorbed amount of DCF increased from 6.29 to 45.96 µg g⁻¹ at pH 5.23, while the adsorbed amount increased from 0.19 to 2.39 µg g⁻¹ at pH 8.84. These phenomena might be explained by the higher utilization of available active sites of goethite at higher DCF concentration. Simultaneously, higher initial concentration of DCF would increase the mass transfer driving force and collision number between DCF molecules and goethite.

As shown in Fig. 2, at different initial concentration of DCF, the trends that the amount of DCF adsorbed to goethite varied with system pH were similar. The amount of adsorbed DCF decreased with the increasing pH. Similar results were reported previously for the adsorption of DCF to other adsorbents (Nam et al., 2015; Thanhmingliana and Tiwari, 2015; Tiwari et al., 2015) and the adsorption of flumequine to goethite (Zhang and Huang, 2007). In our study, the feature of note was that the maximum adsorbed amounts of DCF to goethite were appeared at pH 5.23, which was close to pKₑ (4.15) of DCF. Similar result was found for the adsorption of flumequine to goethite, in which the maximum adsorbed amount of flumequine was gained around pH closed to the pKₑ value of protonation in the carboxyl group (Zhang and Huang, 2007). The adsorption edges of some organic acids (e.g. benzoic, phenylacetic and 3-phenylpropionic) to goethite also showed similar phenomena (Evanko and Dzombak, 1998).

At pH around PZC of goethite, the amount of adsorbed DCF decreased very fast, which was caused by the change in the charges of goethite surface. In the studied pH range (5.0–11.0), DCF existed mostly in its anionic form, and the charges on goethite surface changed with solution pH. At pH < PZC, the positive charges on goethite decreased, and the adsorption of DCF to goethite also decreased linearly. As shown in Table 2, the adsorption of DCF to goethite was fitted well using the Linear model (R² > 0.97). This also supported the conclusion that electrostatic interactions played an important role in the adsorption process at pH (pH < 7). At pH > PZC, goethite and DCF were negative charged, as a consequence, the adsorption was rather weak. The adsorbed amount of DCF was mainly contributed by complexation reaction, which was similar to the adsorption of antibiotics to goethite (Qin et al., 2014a, b; Zhao et al., 2014; Gu et al., 2015). So the amount of adsorbed DCF decreased slowly. And the absolute value of the slope in the Linear model at pH > PZC was an order magnitude smaller than that at

Fig. 1. Effect of reaction time on adsorption of DCF onto goethite. Symbols represent the experimental data, whereas the lines represent the simulated data fitted using the Pseudo-second-order model with the parameters listed in Table 1. Error bars (±1 standard deviation, n = 3) are shown in the figure.
pH < PZC (Table 2). In the adsorption edge of flumequine to goethite, a turning point was observed on the curve at pH value around PZC of goethite, which was opposite to the results in this study. These differences might be caused by the different functional groups between DCF (−COOH and −NH) and flumequine (−COOH and −C=O) (Zhang and Huang, 2007). The complex reaction that occurred between the goethite surface and carboxyl or/and ketone groups in PPCPs was the main adsorption mechanism of PPCPs to goethite (Trivedi and Vasudevan, 2007; Paul et al., 2014; Qin et al., 2014a, b).

3.3. FTIR analysis

Fig. 3 shows the FTIR spectra of DCF and goethite under different pH conditions. DCF had strong absorbance bands such as those at 3388 cm⁻¹ (νN-H), 3257 cm⁻¹ (νN-H-O) due to intermolecular

| Table 1 Sorption rate constants associated with Pseudo-first-order and Pseudo-second-order kinetic models. |
|--------------------------------------------------|--------------------------------------------------|
| **Pseudo-first-order kinetic model**             | **Pseudo-second-order kinetic model**            |
| pH = 5.26 ± 0.09                                 | pH = 5.26 ± 0.09                                 |
| pH = 7.40 ± 0.26                                 | pH = 7.40 ± 0.26                                 |
| pH = 9.96 ± 0.43                                 | pH = 9.96 ± 0.43                                 |
| qe
| 250 mg g⁻¹ | 9.33 | 1.59 | 25.47 | 9.33 | 1.59 |
| 500 mg g⁻¹ | 3.25 | 1.09 | 25.47 | 9.33 | 1.59 |
| 1000 mg g⁻¹ | 155.13 | 5.60 | 1.09 | 25.47 | 9.33 | 1.59 |
| 1500 mg g⁻¹ | 254.48 | 6.60 | 253.92 | 6.67 |
| 2000 mg g⁻¹ | 253.92 | 6.67 |

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FTIR spectrum of DCF showed that the intensity at 1577 cm\(^{-1}\) decreased while FTIR spectra of goethite after adsorption showed that the intensity at 1577 cm\(^{-1}\) increased. This observation suggested that there was chemical complexation between carboxyl groups of DCF and the surface groups of goethite. And proposed types of interaction for DCF complexation on the surface of goethite were bidentate chelate and bridging bidentate complexes (Fig. 4).

Additionally, as shown in Fig. 3(2), the bands (i.e. 1558 cm\(^{-1}\) \(\delta_{\text{N-H}}\), 1508/1500 cm\(^{-1}\) \(\nu_{\text{C=O-arom}}\)) on goethite after adsorption at pH 5.27 (b) were much higher than those at neutral (c) and basic condition (d). This phenomenon supported the conclusion that low pH was beneficial to DCF adsorption on goethite.

4. Conclusion

This work studied the kinetics of DCF upon adsorption to goethite under different pH conditions and the effect of pH on DCF adsorption under different DCF initial concentrations. The sorption kinetic data of DCF at each of three pH values (5.3, 7.4, and 10.0) were fitted well by pseudo-second-order kinetic model. Adsorption of DCF on goethite was greatly influenced by pH in solutions, and more DCF was adsorbed on goethite at low pH according to pH-edge adsorption experiments. Electrostatic interactions can contribute to the overall sorption. FTIR results supported that there was chemical complexation between carboxyl groups and the surface groups of goethite. And proposed types of interaction for DCF complexation on the goethite were bidentate chelate and bridging bidentate. The results acquired in the study help us to better estimate the distribution and mobility of similar ionization pharmaceuticals in the environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.04.007.