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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 depended on solution pH. The amount of adsorbed DCF decreased with increasing pH duo 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.

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 (Scheytt et al., 2004; Yu and Bi, 2015). Previous studies showed that DCF was retarded (Retardation factor = 2.0) in the soil column

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(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 (f_{oc}) 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 (Paul 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 $C_{14}H_{10}Cl_2NNaO_2$, and the molecular weight is 318.14. The protonation constant (pK_a) 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}, $I = 0.01$ 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 taken after shaking for 5 min, 10 min, 20 min, 45 min, 67 min, 130 min, 240 min, 480 min, 720 min, 1440 min, and 2880 min. Then the samples were centrifuged at 3000 rpm for 15 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:

$$q_t = \frac{V(C_0 - C_t)}{M} \tag{1}$$

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):

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{2}$$

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

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

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, Gangdong, Tianjin), operating in the wavenumber range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Sixteen scans were collected and averaged for each sample and background to get the spectrum.