Sorption kinetics, isotherms, and mechanism of aniline aerofloat to agricultural soils with various physicochemical properties

Lei Xiang[a], Tao Xiao[a], Ce-Hui Mo[a,*], Hai-Ming Zhao[a], Yan-Wen Li[a], Hui Li[a], Quan-Ying Cai[a], Dong-Mei Zhou[a,b], Ming-Hung Wong[a,c]

[a] Guangdong Provincial Research Center for Environment Pollution Control and Remediation Materials, College of Life Science and Technology, Jinan University, Guangzhou 510632, China
[b] Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
[c] Consortium on Health, Environment, Education and Research (CHEER), Department of Science and Environmental Studies, Institute of Education, Tai Po, Hong Kong, China

ARTICLE INFO

ABSTRACT

Aniline aerofloat (AAF), a high-toxic organic flotation reagent, is widely used in mineral processing industry. However, little information on its environmental fate is available. AAF sorption to four types of agricultural soils at low concentrations (1–10 mg/L) was investigated using batch experiments. AAF sorption kinetics involved both boundary layer diffusion and intraparticle diffusion, following pseudo-second-order kinetics with equilibrium time within 120 min. Both Langmuir and Freundlich models fitted well the AAF sorption with the former better. Sorption of AAF to soils was a spontaneous and favorable physical sorption that was controlled by ion bridge effect and hydrophobic interaction that was related to van der Waals force and π-π coordination based on FTIR analyses. AAF sorption was remarkably affected by soil constituents, positively correlating with the contents of organic matter and clay. The relatively higher $logK_{oc}$ values (3.53–4.66) of AAF at environmental concentrations (1–5 mg/L) imply that soils are serving as a sink of AAF from beneficiation wastewater, posing great potential risks to environment and human health.

1. Introduction

With the increase of mining activities around the world, numerous pollutants such as heavy metals (HMs) (Yang et al., 2010; Geranian et al., 2013), acid mine drainage (AMD) (Mahiroglu et al., 2009; Torres et al., 2013), radioactive substances (Villa-Alfageme et al., 2011), and flotation reagents (Gredelj et al., 2009; Reyes-Bozo et al., 2011) have been released into environment, causing various ecological issues. For example, world-shocking itai-itai disease in Japanese Kamioka mine area was developed by chronic cadmium poisoning owing to mining activities (Inaba et al., 2005). A village near Dabao Mountain mine area in Guangdong province, southern China was termed endemic "cancer village" with high cancer incidences due to long-term exposure of human body to multiple pollutants originating from large-scale mining activities (Zhuang et al., 2009; Wang et al., 2011). Contamination in mining districts has become a major environmental concern. However, the previous studies about mining pollutants almost focused on HMs or AMD, and little information on organic flotation reagents is available.

Various organic flotation reagents such as aerofloat, xanthate, and quaternary ammonium compounds are extensively used to separate, extract or purify valuable metals during mineral processing, resulting in numerous wastewater containing organic flotation reagents (Hissner et al., 1999; Sis and Chander, 2003; Xiang et al., 2014; Lin et al., 2017). For examples, more than 1.2 billion cubic meters of floatation wastewater are produced annually in China (Lin et al., 2017). Correspondingly, various organic flotation reagents are found in environmental media including wastewater, surface water, irrigation water, soil and municipal sludge (Xiang et al., 2014; Zheng et al., 2014; Lin et al., 2017). Recently, aerofloat was detected with concentrations of 0.45–1.43 mg/L in the waters from mining districts of Daobao Mountain (Supplementary data, Table S1). It is noted that aerofloat could not be effectively eliminated in the sewage treatment plant that aimed to treat heavy metal-polluted water from Daobao Mountain mining area. Therefore, more than 70% of aerofloat in influent was released via the effluent to Hengshi River nearing the sewage treatment plant, and mg/L level of aerofloat was detected in irrigation water from downstream of the river, posing a great ecological risks to agricultural soil. Generally, the organic flotation reagents exhibit moderate and even high toxicity

(Luan and Yao, 2002; Huang et al., 2011; Lin et al., 2017), and their residues in environment can cause significant negative effects, e.g. inhibition of the growth and reproduction of fish at low concentration (several mg/L) and alteration of microbial community dynamics in activated sludge at relatively high concentration (Xu et al., 1988; Boening, 1998; Lin et al., 2017). Accordingly, investigations on the environmental behaviors of organic flotation reagents are urgently needed.

Soils usually serve as important sink of organic pollutants. The sorption behaviors of organic pollutants in soils determine their bioavailability, mobility, and environmental fate (Pateiro-Moure et al., 2010; Xiang et al., 2016). Furthermore, the sorption of or organic pollutants is closely related to their ecological risks (Kim et al., 2012; Xiang et al., 2016). Surface water containing organic flotation reagents could be used as irrigation water, causing negative effects on soil ecosystem (Xiang et al., 2014; Zheng et al., 2014). However, there is hardly research on sorption of organic flotation reagents to soils up to now.

Aniline aerofloat (AAF) is a typical aerofloat with several advantages including low cost, simple production process, and strong complexation with valuable metals (Luan and Yao, 2002). It is widely used in the flotation of galena, sphalerite, and chalcopyrite, etc. in China (Song and Deng, 2012). Numerous AAF is discharged into environment (especially the river water) via beneficiation wastewater (Lin et al., 2016a). AAF is toxic to organism by the non-specific inhibition of the enzyme acetylcholinesterase in the nervous system owing to its dithiophosphate groups (Yao et al., 2010; Lin et al., 2016a). Furthermore, AAF could release iminobenzene radicals, aniline or other polyaniline derivatives under the action of light or microorganism, resulting in remarkable negative effects on environment (Lin et al., 2016a). Additionally, AAF has been proven to be a partially degradable organic compound, and it is not easily biodegradable (Lin et al., 2016b). Considering the ubiquitous occurrence, high toxicity, and stronger stability of AAF in environment, its environmental behaviors especially for sorption behavior are eagerly needed to be evaluated.

Therefore, AAF was chosen as a representative compound of the organic flotation reagent at relatively lower concentrations (1–10 mg/L) to investigate its sorption to various agricultural soils using batch equilibrium experiments. At the same time, the effects of the physical and chemical properties of the soils and the common ions (Na^+, Mg^{2+}, Cl^-, and SO_4^{2-}) in water solutions on the AAF sorption were evaluated. Furthermore, the Fourier transform infrared spectroscopy (FTIR) and a dual isotherm model were performed to reveal the mechanism of AAF sorption. To the best of our knowledge, this is the first study on AAF sorption to the soils, which is beneficial to understand the sorption behavior of AAF in water-soil interface, and provide environmental implications in the aspect of fate and transport of AAF in agricultural soils.

2. Experimental

2.1. Soils and chemicals

Four characteristic and uncontaminated agricultural surface soils (0–20 cm) were collected and labeled by Soil A, Soil B, Soil C, and Soil D. Soil A was sampled from Jilin province in northeast China, and the others were sampled from Guangdong province in southern China. Soil A and Soil C were chosen as representatives of submerged soil, while Soil B and Soil D were selected as the coastal soil and upland soil, respectively. All the sampled soils were freeze-dried, sieved through a 2-mm of stainless steel sieve, and then stored at 4 °C for further use. The main physical-chemical properties of the soils were determined by the recommended soil testing procedures (Lu, 2000), with the results as follows: pH value (4.80–6.54), cation exchange capacity (CEC, 7.1–154 cmol/kg), organic matter content (OM, 0.76–5.26%), phosphorus (P, 0.20–1.03 g/kg), potassium (K, 5.8–22 g/kg), sand content (24.1–48.2%), silt content (32.2–44.9%), and clay content

(19.6–31.0%) (Supplementary data, Table S2).

Aniline aerofloat (AAF) with 95% purity was purchased from the Zibo Dayang Chemical Reagents Co. Ltd., China. Its molecular formula, weight, and oil-water partition coefficients (logP) were $(C_6H_5NH)_2PSSH$, 280 g/mol, and 3.56, respectively (Supplementary data, Fig. S1). The Stock solution of AAF (100 mg/L) was freshly prepared by adding AAF to deionized water with 0.01 mol/L NaOH (to ensure AAF dissolved sufficiently) and stored in a brown volumetric flask at 4 °C in the dark. All other chemical reagents purchased from Guangzhou Chemicals Reagents Co. Ltd., China were of analytical grade.

2.2. Batch sorption experiments

Batch sorption experiments were carried out following the OECD Guideline 106 (OECD, 2000). In short, 0.25 g soils and 25 mL AAF solution (1–10 mg/L) containing 0.01 mol/L $CaCl_2$ and 0.3% NaN_3 were added into 50 mL Teflon-lined centrifuge tubes. The $CaCl_2$ and NaN_3 were used to keep constant ionic strength and inhibit microbial activities, respectively. After mixed for 30 s, the tested tubes were shaken at 250 rpm and at 25 ± 1 °C for 1–960 min, and then centrifuged at 8000 rpm for 5 min. The AAF concentrations in supernatants were measured by spectrophotometric method, and the amounts of AAF adsorbed to soils were calculated from the concentration differences using the following Eq. (1):

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

where q_t (mg/g) and c_{surf} (mg/L) are concentrations of AAF in soils and supernatants at the sampling time, respectively, c_0 is initial concentration of AAF in the sorption experiment (mg/L), v is AAF solution volume (0.025 L), and m is soil mass (0.25 g). Preliminary experiments showed that AAF loss was negligible due to volatilization, microbial activity, and sorption by the centrifuge tube, as well as AAF desorption from original soils during the sorption experiment.

In sorption kinetics experiment, AAF concentration was set at 10 mg/L. Supernatants were sampled for AAF determination at thirteen time intervals (1, 5, 10, 20, 30, 40, 50, 60, 90,120, 240, 480 and 960 min). Sorption equilibrium time of AAF to soils was determined by the sorption kinetics experiment. In sorption isotherm experiment, initial concentrations of AAF were set as 1, 2, 5, 8 and 10 mg/L, respectively. According to previous studies, sorption equilibrium time of an organic compound at a lower concentration was shorter than that at a higher concentration (Ismail et al., 2010; Xiang et al., 2016). Therefore, the sorption equilibrium time (120 min) of AAF at 10 mg/L obtained from kinetics experiment was sufficient for use at lower concentrations (< 10 mg/L), and thus it was set as the sampling time for AAF determination in the isotherm experiment. All experiments were conducted in triplicates.

2.3. Analytical methods

2.3.1. AAF determination

AAF concentrations were determined according to the method described in a previous literature with little modification (Huang et al., 2011). Briefly, water sample (20 mL) was diluted to 100 mL with deionized water in a 250 mL of separatory funnel. Afterwards, 10 mL acetic acid-sodium acetate buffer solution (pH = 5.2) and 5 mL copper sulphate solution (0.01 mol/L) were added into the separatory funnel. After mixed, the solution stood for 5 min and then was extracted by 5 mL n-hexane. Subsequently, the n-hexane phase was rinsed by 30 mL deionized water twice. The AAF concentration in n-hexane extract was measured at 432 nm wavelength against n-hexane blank on a UV–vis spectrophotometer, and the AAF concentration in supernatant could be obtained based on the AAF concentration in the n-hexane phase. The limit of quantification (LOQ) for AAF was 0.01 mg/L. The spiked blanks (solvent spiked with standards) and spiked supernatants (1–10 mg/L of