Chemosphere 197 (2018) 291–298

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effects of Fe(III)-fulvic acid on Cu removal via adsorption versus coprecipitation

Ren Yang [a, b], Zhongwu Li [a, b, *], Bin Huang [c], Ninglin Luo [a, b], Mei Huang [a, b], Jiajun Wen [a, b], Qiu Zhang [a, b], Xiuqing Zhai [a, b], Guangming Zeng [a, b]

[a] *College of Environmental Science and Engineering, Hunan University, Changsha, 410082, PR China*
[b] *Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, 410082, PR China*
[c] *Guangdong Key Laboratory of Integrated Agro-environmental Pollution Control and Management, Guangdong Institute of Eco-environment Science &Technology, Guangzhou, 510650, PR China*

HIGHLIGHTS

- The ternary precipitates were formed and Cu(II) removal by adsorption and coprecipitation was compared.
- More Cu was removed as the pH increased in the ternary system.
- The additional FA remarkably increased Cu concentrations during SOR reactions.
- Extractability of Cu was generally lower from coprecipitates.

ARTICLE INFO

Article history:

Handling Editor: Patryk Oleszczuk

Keywords:
Ferrihydrite
Copper
Fulvic acid
Adsorption
Coprecipitation

ABSTRACT

This study compared the sorption and extractability of Cu following adsorption (SOR) and coprecipitation(CPT). The effect of solution pH, Fe: organic carbon (OC) ratios and fulvic acid (FA) on the combined removal of Cu was investigated in the batch tests using Fe(III) precipitates as a sorbent. Transmission electron microscope (TEM) images demonstrated that the coexisting FA reduced the particle size of ferrihydrites as expected. Generally, more Cu was eliminated in coprecipitation compared with adsorption and the dissolved Cu left in solutions decreased as the pH increased, most of dissolved Cu was trapped at pH 6 and above. Meanwhile, the inhibition or promotion of Cu removal really depended on the different Fe: OC ratios. The addition of FA led to a further decrease of Cu concentrations in CPT systems with Fe/OC ratio of 1:3, however, Cu removal was hindered in the presence of FA in SOR systems. In the case of extraction experiments, the addition of L-malic acid (MA), oxalic acid (OA) and citric acid (CA) resulted in lower extractability of coprecipitated Cu than adsorption samples. The gaps in extractions were seemed to be a consequence of tight Cu binding in CPT products, and the more feasible desorption of Cu from the surface of SOR samples. Based on the results of Cu adsorption and coprecipitation, coprecipitation of Cu with ferrihydrites was the more effective Cu sequestration mechanism in the removal of Cu. These results are helpful to understand the complicated interactions among Fe(III), FA and Cu (II) in the natural environment.

1. Introduction

Competing phases in natural soil and aquatic systems such as iron (hydr)oxides and organic matters (OM) have been widely considered to largely impact the environmental behaviors of dissolved metal ions (Huang et al., 2014; Cornell and Schwertmann, 2003; Zhang et al., 2017), and the continuous release of the competing phases into the environment is causing more and more public concerns (Deng et al., 2013; Xu et al., 2012; Li et al., 2017). Iron oxides formed extensively in surface environments and have high efficiency for eliminating trace metals (Jambor and Dutrizac, 1998). Poorly crystalline Ferrihydrite is generally the first solid phase during precipitation, which in particular is known for changing free metal and OM concentrations in aqueous system

---

* Corresponding author. College of Environmental Science and Engineering, Hunan University, Changsha, 410082, PR China.
E-mail address: lizw@hnu.edu.cn (Z. Li).

https://doi.org/10.1016/j.chemosphere.2018.01.042
0045-6535/

through adsorption and coprecipitation (Lai et al., 2002). As a nanoparticle, ferrihydrite is usually less than 10 nm in diameter (Hochella et al., 2008), accordingly they act as an effective scavenger of contaminants due to their large surface area and strong sorption properties.

Humic substances (HS) are present ubiquitously in natural aquatic ecosystems, with high reactivity and strong binding capacity, exerting great influence in changing surface properties, aggregation, transportation of nanomaterials and controlling retention and availability of harmful metals in the environment (Tang et al., 2014). Besides, it has been well discussed that the intimate associations of iron minerals with organic components can alter the crystallization and particulate size of the newly formed iron oxides (Schwertmann et al., 2005a; Mikutta, 2011), However, compared to the well-studied interactions between humic acid (HA) and iron oxides (Liu et al., 2008a; Catrouillet et al., 2016), very few studies have examined the impact of fulvic acid (FA) which is the major composition of humic substance and has lower molecular weight and contains more functional groups relative to humic acid (Güngör and Bekbölet, 2010). Additionally, the effect of HA/FA on the removal of heavy metals by iron oxides was dependent on HA/FA concentrations and pH values (Dong et al., 2010), and this multi-phase system involved a complicated process, either positive effects or suppressive effects of HS were reported for iron nanomaterials treatment (Liu et al., 2008b; Davis and Bhatnagar, 1995; Huang et al., 2016). Therefore, to find out the effect of HS onto the surface of iron oxides and further removal of hazardous metals, it is necessary and important to identify the behavior and influence of HS sorption onto the iron particle adding metal ions.

In natural waters, the formation of ferrihydrites commonly occurs in the presence of dissolved organic matter (DOM), which results in the coprecipitation of OM with ferrihydrites. Unlike the pollutants added to a suspension where OM adsorbed to already existing Fe hydrous oxides in adsorption experiments, in actual environment, metals are present in the solution when OM and iron precipitates to form coprecipitates (Mikutta et al., 2008). The formation of ferrihydrite coprecipitates exhibited fewer crystal planes, increased lattice spacings and smaller particles as Fe/C ratios of the initial solution decreased. Even low doses of OM could clearly impact on the structure of solid phases. (Eusterhues et al., 2008). The reactivity of Fe minerals can thus directly affected by interaction of organic matter during Fe precipitation due to their participation in adsorption (Liu and Huang, 2003) and dissolution (Mikutta and Kretzschmar, 2008). In addition, Cu release from wetlands have been correlated to a combination of colloidal iron oxides and/or OM release, which indicates the role of both solid phases in controlling Cu release (Grybos et al., 2007) Another study on arsenic proved that As^{3+} can be retained by either adsorption or coprecipitation to the surface of iron oxides (Courtin-Nomade et al., 2005). Despite this, little is known about the impact of different contact methods on metal removal, and understanding the underlying differences is important for predicting the fate of embedded metals such as Cu.

Hence, the objective of present work is to (1) evaluate the difference of Cu attenuation via comparing the adsorption of Cu on the surface of iron oxides and the coprecipitation of Cu with iron oxides in the presence or absence of FA; (2) elucidate the impacts of fulvic acid on the fate of Cu in ternary system. Fe minerals were formed under different Fe: OC and pH, as well as the net Cu sorption was examined through SOR or CPT reactions. Precipitates were collected and then assessed the availability of Cu based on a series of extractions by three representative organic ligands. A clear understanding of these intricate interactions is thus crucial to fully illustrate the fate and transport mechanisms of iron colloids and Cu in the environment.

2. Materials and methods

2.1. Reagents and materials

A commercial and standardized FA purchased from Anhui ahkuer bio-technology co. LTD was chosen as a model for organic matter. FA stocks were prepared by dissolving in 10 mM $NaNO_3$ with magnetic stirring for 24 h and stored at 4 °C in the dark. The dissolved organic carbon concentration was measured prior to experimental use. Cu(II) and Fe(III) solutions were prepared from $CuSO_4 \cdot 5H_2O$ and $FeCl_3 \cdot 6H_2O$, respectively. Fe(III) aqueous solutions were maintained at $pH = 2$ to avoid precipitation of iron oxides. For all experiments, ionic strength was fixed by 10 mM $NaNO_3$ as well as pH was adjusted by the addition of 0.1 M HCl and NaOH. 18 MΩ ultrapure water was applied to the preparation of any solutions and containers were acid soaked in 10% HNO_3 for 24 h before experiments. In addition, all experiments were conducted in triplicate and chemicals used in this study were of analytical grade.

2.2. Coprecipitation (CPT) and adsorption (SOR) reactions

The formation of iron oxide in the presence of Cu ions occurred during the precipitation reactions. To accomplish this, 50 mL triplicate solutions of coprecipitation experiments were prepared in centrifuge tube with 10 mM $NaNO_3$ background solutions, and the initial Cu(II) concentration was fixed at 2 mg/L, which is much higher than the national water quality standard (GB3838-2002) of China. Then added the FA solutions at 0, 25, 84 mg/L organic carbon to give initial Fe: OC molar ratios at 1:0,1:3 and 1:10, which were the typical ratios mentioned by Seda et al. (Seda et al., 2016). Finally, the Fe(III) added at a constant concentration of 40 mg/L, after which the pH was adjusted from 2 to 10 (2, 4, 6, 8, 10) to form Fe(III) precipitates by the addition of a few drops of NaOH. The suspensions were then shaken on a constant temperature bath oscillator at 110 rpm under out light condition and, controlling the pH within ±0.2, for 1 h. All samples continued to shake for 24 h, at room temperature (25 °C). The mixture was centrifuged at 4000 rpm for 30 min and filtered through a 0.22-μm membrane filter. The obtained solid precipitates were dried overnight in an oven at 75 °C for 24 h and then the dry mass was weighed. The residual concentrations of Cu and Fe of the filtrates were determined using an ICP-OES (Optima 5300DV; Perkin Elmer, USA), and the DOC was determined by measuring on a TOC analyzer (Shimadzu Corp., Kyoto, Japan).

For comparison with the coprecipitation experiments, adsorption experiments were conducted using the same conditions as for the coprecipitation experiments, but oscillated for 24 h without the initial addition of Cu. After that, 2 mg/L Cu(II) was added and both the pH values and ionic strengths of experimental solutions were adjusted to the target levels. The samples were then shaken for an additional 24 h. Following oscillation, all suspensions were centrifuged and filtered consistent with the above-mentioned conditions prior to the measurements elemental analysis.

2.3. Determination of extractable Cu by organic ligand from CPT and SOR products

In order to assess the extractability and availability of Cu within the products, L-malic acid, oxalic acid and citric acid were sequentially used to extract the exchangeable, complexed, adsorbed and coprecipitated forms of Cu from SOR and CPT precipitates, and then to investigate the impacts of coexisting FA on metal mobility. A mass of (1 L) CPT and SOR stocks were prepared with