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A novel biodegradable arsenic adsorbent by immobilization of iron oxyhydroxide (FeOOH) on the root powder of long-root *Eichhornia crassipes*

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HIGHLIGHTS

- MRP showed great adsorption performance for As(V) and As(III).
- FeOOH formed on RP had better dispersion, stability and arsenic adsorption.
- The application of long-root *Eichhornia crassipes* was developed further.

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ABSTRACT

In this study, FeOOH was immobilized on the biodegradable root powder, abbreviated as RP, of long-root *Eichhornia crassipes*, a kind of waste biomass, to improve the adsorption performances for aqueous arsenic contaminants. The adsorption kinetics and thermodynamics experiments showed that the adsorption rates and capacities of the root powder for arsenate (As(V)) and arsenite (As(III)) were both enhanced markedly after modification with FeOOH. The adsorption of As(V) and As(III) by the modified root powder, abbreviated as MRP, could arrive at equilibrium in 50 min and the saturated adsorption capacities reached up to 8.67–9.43 mg/g for As(V) and 5.21–5.65 mg/g for As(V) at temperature of 10–50 °C, respectively. Besides, the effect of pH and ionic strength on adsorption was investigated and the results showed that the optimum pH for the arsenic adsorption using the MRP was 9.0 and the As(V) adsorption was more sensitive to ionic strength. Furthermore, the complexation of hydratable hydroxyls on FeOOH with arsenic contaminants was concluded as the adsorption force according FTIR and XPS analyses. The MRP used could be regenerated via 0.4 mol/L NaOH solution and no apparent adsorption capacity losses appeared after 6 cyclic utilizations.

1. Introduction

In recent years, arsenic pollution in water, as known as a deadly poison since ancient times due to its lethality, has become a serious problem on account of its adverse effects on ecological systems and human health, mainly stemming from natural or human induced activities including mining(Krysiak and Karczewska, 2007), pesticides(Mandal and Suzuki, 2002) and feed industry(Rodriguez-Lado et al., 2013), *etc*(Ma, 2013; Pierce et al., 2013; Farooq et al., 2016). Fortunately, nowadays various treatments of arsenic-contaminated water have been developed such as chemical precipitation(Janin et al., 2009a), ion-exchange(Singh et al., 2015), membrane separation(Košutić et al., 2005), electrolysis(Janin et al., 2009b; Renock and Voorhis, 2017), biosorption, adsorption and so on(Warren et al., 2003; Sharma and Sohn, 2009; Tuček et al., 2017). Among them, adsorption is one of the most extensively investigated methods due to its cost-effectiveness and convenience of subsequent processing(Jiang, 2001; Bissen and Frimmel, 2003; Mohan and Pittman, 2007; Lin et al., 2012a, 2012b; Thommes and Cychosz, 2014; Andjelkovic et al., 2015). Therein, materials with biodegradability and cost performances, have been extensively utilized as arsenic adsorbents recent years while relentless efforts

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are still required to improve the adsorption capacity to satisfy the application in wastewater treatment(Kamala et al., 2005; Pokhrel and Viraraghavan, 2006; Sari et al., 2011; Lin et al., 2012b; Yang et al., 2015; Maneerung et al., 2016). Long-root *Eichhornia crassipes*, distinguished by its long root accounting for more than 80% of its biomass, has showed great remediation effect under the test to treat Dianchi Lake in China suffering from eutrophication depending on its extraordinary uptake of aqueous nitrogen and phosphorous, while how to dispose these massive plants reaped from Dianchi has been another pressing challenge(Li et al., 2013). In previous study, we discovered the root powder of long-root *Eichhornia crassipes*, possessing multiple functional groups on the surface including hydroxyl (-OH), amine (-NH_2), carboxyl (-COOH), *etc*, as a kind of biodegradable adsorbent, had the potential to remove arsenic compounds from wastewater(Lin et al., 2012b). However, similar to most bio-adsorbents, the adsorption capacity for arsenic contaminants of the root powder are far from sufficient, which has been the bottleneck to hinder the application of root powder in wastewater treatments though it has excellent availability and biodegradability. Hence, it is crucial to improve the adsorption capacity of the root powder with simple methods, concerning to provide an ecologically friendly way to deal wastewater with arsenic and recycle the long-root *Eichhornia crassipes* as a kind of available resource. According to Grossl's study(Grossl et al., 1997), FeOOH had excellent adsorption ability to arsenic species due to plenty of hydratable hydroxyl groups on surface forming inner-sphere complexes with As(V) or As(III) while the innate properties of metastability and aggregation in solution have hindered its comprehensive availability. Therefore, in this study, in view of the features of FeOOH and the root powder (RP), we synthesized and immobilized FeOOH on the RP surface to enhance the stability and dispersion of FeOOH as well as the adsorption capacity of the RP for arsenic contaminants. Subsequently, the physicochemical properties of the modified root powder (MRP) were examined in detail by diversified measurements including FTIR, SEM, EPS, TG, XRD, *etc*. And the effect of initial pH and ionic strength was analyzed as well as the adsorption dynamics and thermodynamics for arsenic in different conditions. Meanwhile, the detailed appraisal of arsenic compounds on to the MRP were also investigated with particular focus on the adsorption mechanism. Base on the adsorption performance obtained, the remarkable improvement on the adsorption capacity for As(V) and As(III) was confirmed, which was essential to embody the effectiveness of the method to modify the root powder of long-root *Eichhornia crassipes* and offer explicit direction towards its future application in the wastewater treatment industry.

2. Experimental section

2.1. Materials and reagents

All chemicals used in experiments in this study were of analytically pure grade without further purification. $FeCl_3 \cdot 6H_2O$, HCl, HNO_3, NaCl and NaOH were all purchased from Modern Oriental Fine Chemicals Co., Ltd. And $NaH_2AsO_4 \cdot 12H_2O$ and $NaAsO_2$ were provided by Sinopharm Chemical Reagent Co., Ltd. Standard arsenic solutions were received from the National Institute of Metrology (Beijing, China). The root powder of long-root *Eichhornia crassipes* with the particle size of 300–600 μm was applied as the source of the MRP. The arsenic stock solution (1 g/L) was prepared by dissolving $NaH_2AsO_4 \cdot 12H_2O$ or $NaAsO_2$ in ultrapure water. The As(V) or As(III) solutions used in experiments were prepared by diluting the stock solution with deionized water. All glassware was soaked in 15% HNO_3 and washed with deionized water three times before use. In all experiments, the initial pH values of solutions were adjusted by using 0.05 mol/L HCl and 0.05 mol/L NaOH.

2.2. The MRP preparation

FeOOH was immobilized on the RP surface to prepare MRP via an impregnation and coagulation process. Specifically, 1 g RP washed with deionized water, was dispersed in 200 mL solution with 0.1 mol/L Fe^{3+} ($FeCl_3 \cdot 6H_2O$) at pH value of 3.0. Then the suspension was set in a shaker (SPH-103B, SHIPPING, China) for

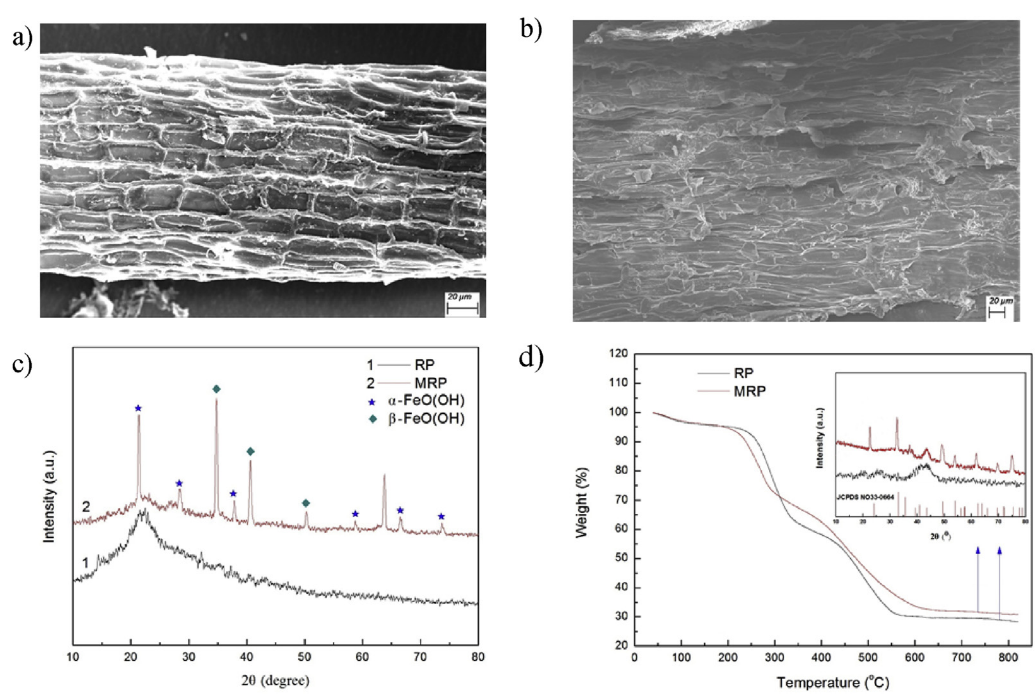

Fig. 1. Typical SEM images of RP (a) and MRP (b); XRD patterns of RP and MRP (c); TG analysis of RP and MRP (d).