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Competitive sorption of heavy metals by water hyacinth roots

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ABSTRACT

Heavy metal pollution is a global issue severely constraining aquaculture practices, not only deteriorating the aquatic environment but also threatening the aquaculture production. One promising solution is adopting aquaponics systems where a synergy can be established between aquaculture and aquatic plants for metal sorption, but the interactions of multiple metals in such aquatic plants are poorly understood. In this study, we investigated the absorption behaviors of Cu(II) and Cd(II) in water by water hyacinth roots in both single- and binary-metal systems. Cu(II) and Cd(II) were individually removed by water hyacinth roots at high efficiency, accompanied with release of protons and cations such as Ca^{2+} and Mg^{2+}. However, in a binary-metal arrangement, the Cd(II) sorption was significantly inhibited by Cu(II), and the higher sorption affinity of Cu(II) accounted for its competitive sorption advantage. Ionic exchange was identified as a predominant mechanism of the metal sorption by water hyacinth roots, and the amine and oxygen-containing groups are the main binding sites accounting for metal sorption via chelation or coordination. This study highlights the interactive impacts of different metals during their sorption by water hyacinth roots and elucidates the underlying mechanism of metal competitive sorption, which may provide useful implications for optimization of phytoremediation system and development of more sustainable aquaculture industry.

1. Introduction

Environmental water deterioration caused by modern aquaculture activities has become a severe global challenge today (Sapkota et al., 2008). Especially, the increased use of pelleted feed has led to intensified eutrophication and heavy metal pollution of aquatic environment (Farmaki et al., 2014). This in turn affects the aquaculture production practices, where various external toxic chemicals accumulate in aquatic organisms and deteriorate the product quality and security (Bostock, 2011; Mendoza-Carranza et al., 2016). As a potential solution, aquaponics systems based on the integration of conventional aquaculture with aquatic plants cultivation have attracted great attention recently. In such systems, the aquatic plants can absorb large amounts of nitrogen, phosphorus and various heavy metals from the contaminated water through a process called phytoremediation (Rezania et al., 2015b), thereby minimizing the environmental discharge of aquaculture or even enabling a recirculating aquaculture system (Deng et al., 2004). Meanwhile, the aquaculture wastes can effectively fertilize aquatic plants and promote their growth (Medina et al., 2016).

Water hyacinth is considered as a promising aquatic plant for aquaponics, attributed to its good ability for absorbing pollutants, superior tolerance to contaminated environment, rapid growth (Mahamadi and Nharingo, 2010b; Zhang et al., 2014) and high economic value with diverse potential applications (Rezania et al., 2015a). In particular, due to its superior heavy metal sorption and accumulation abilities compared to most other aquatic macrophytes (Malik, 2007), water hyacinth has gained widespread interest in environmental phytoremediation applications (Chunkao et al., 2012; Gupta and Balomajumder, 2015; Rezania et al., 2015b).

It has been well-established that water hyacinth, especially its roots, possesses a strong ability to remove heavy metals from aqueous solution, with the sorption performances vary depending

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on the metal species, concentration and solution chemistry (Gupta and Balomajumder, 2015; Hasan et al., 2007). A high sorption of heavy metals, such as cadmium (Cd), zinc (Zn), chromium (Cr), lead (Pb), and copper (Cu), by water hyacinth or its routs have been demonstrated in previous studies (Hasan et al., 2007; Hu et al., 2007; Ibrahim et al., 2012; Low et al., 1994; Mitra et al., 2014; Zheng et al., 2009). Importantly, the sorption of different metals could be affected by each other, which is considered an important reason accounting for the usually large discrepancies in various sorption studies in complex natural water systems. Due to the very strong metal sorption and accumulation ability of the root relative to other parts of water hyacinth (Mishra et al., 2008), the competitive sorption of multiple metals by dried water hyacinth have been specifically investigated in several previous studies. Hasan et al. (2007) investigated the sorption of metal mixture by water hyacinth root and found a higher accumulation of Zn(II) over Cd(II). Studies by Mahamadi and Nharingo (2010a) showed that the sorption of Cd(II) and Zn(II) were suppressed by of Pb(II). Cu(II) was recently shown to also suppress the sorption of Cd(II) and Zn(II) by dehydrated root powder of a long-root water hyacinth (Li et al., 2016), indicating that competitive sorption of metals by water hyacinth is a universal phenomenon in natural aquatic system. However, studies in this respect are scattered and the underlying mechanisms of such sorption competition among different metals are still unclear so far.

Given the complexity of aquaculture system where multiple metals typically coexist, it is essential to clarify the interactions of different metals during their absorption by water hyacinth roots, which is an unaddressed issue so far. In this work, we examined the competitive sorption of Cd(II) and Cu(II) ions by water hyacinth roots by taking full consideration of the ion concentration, influential factors and the sorption and desorption properties. The Cd(II) and Cu(II) ions are selected here because they are ubiquitous in various aquatic environment especially in China and are prone to bioaccumulation (Del Toro et al., 2010; Meng et al., 2016; Wu et al., 2012), thereby severely threatening the aquatic ecosystem and the aquaculture industry. For comparison, the individual sorption of Cd(II) or Cu(II) was investigated under identical conditions as binary-system test. Such a comparison between single- and binary metal systems can clearly reveal valuable information as to how the sorption of multiple metal ions is mutually affected. In addition, we shed light on the mechanisms of such metal competitive sorption. The findings in this work can lead to a better understanding on the metal competitive sorption behaviors of water hyacinth, and may provide valuable implications for optimized control of aquaponics systems and development of more sustainable aquaculture industry.

2. Materials and methods

2.1. Preparation of water hyacinth roots

Water hyacinth used in this work was obtained from a river in Suzhou, China. The water hyacinth roots were separated from the plant and thoroughly washed 5 to 7 times with tap water, followed by rinsing in deionized water. The cleaned roots were dried at 70 °C until constant weight. Reagent-grade $CuCl_2 \cdot 2H_2O$, $CdCl_2 \cdot 2H_2O$, HCl and NaOH purchased from Sinopharm Chemical Reagent Co., Ltd were used to prepare the test solutions.

2.2. Experimental set-up

The dried water hyacinth roots were activated in deionized water for 6 h before sorption experiments. In the batch tests of single-metal sorption experiments, 20 mg of roots was added into 50 ml Cu(II) or Cd(II) solution at different initial concentrations. The solution pH was adjusted to 5.50 ± 0.05 with HCl and NaOH solutions. The mixtures were sealed and shaken at 150 rpm at 298 K for 10 h to ensure sorption equilibrium.

In the binary-metal sorption experiments, 50 ml of a Cu-Cd mixed solution was used. The initial concentration of Cu(II) ions was fixed at 0.472 mmol L^{-1} while the concentrations of Cd(II) varied between 0 and 0.356 mmol L^{-1} to test the impact of Cd(II) on Cu(II) sorption. In another test, the Cd(II) initial concentration was fixed at 0.267 mmol L^{-1}, while the Cu(II) concentration varied between 0 and 0.629 mmol L^{-1} to study the inverse process. Studies of pH effects on competitive sorption were carried out with 0.472 mmol L^{-1} Cu, 0.267 mmol L^{-1} Cd. Such different mole concentrations of Cu and Cd were chosen because they represent the same mass concentration, and these two initial concentrations of metals (i.e., 0.472 mmol L^{-1} for Cu(II) and 0.267 mmol mg L^{-1} for Cd(II)) were adopted in the sorption experiments unless otherwise specified. For characterization of the competitive sorption kinetics, morphology and chemical composition of the roots, 50 mg of roots and 100 ml of solution were used. In all the other sorption experiments, 20 mg of roots and 50 ml of solution were used.

Cd-sorbed roots were obtained by soaking the water hyacinth roots (20 mg) in 50 ml Cd solution (0.267 mmol L^{-1}) for 12 h, followed by rinsing with deionized water and drying at 70 °C. Cu-sorbed roots were prepared in similar way with 50 ml Cu solution (0.472 mmol L^{-1}). Both Cd-sorbed and Cu-sorbed water hyacinth roots were analyzed by X-ray photoelectron spectroscopy (XPS). Cd desorption experiment was conducted by adding 20 mg of Cd-sorbed roots in 50 ml of Cu solution (0.472 mmol mg L^{-1}) or deionized water.

All experiments were carried out at 25 °C in a temperature-control shaker. Solution pH was recorded by a pH meter (Mettler Toledo, Germany). Except for studying the pH effects, the solution pH in all experiments was adjusted to 5.50 ± 0.05. The concentrations of metal species were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Optima 2100 DV, Perkin Elmer, USA). During the course of the biosorption, aliquot of 1.0 ml was removed from the solution at regular intervals and diluted with 2% HNO_3 solution for the metal concentration measurement.

2.3. Morphology and composition characterization of the water hyacinth roots

The surface morphology and element composition of the roots after adsorption in the single- and binary metal systems as well as in the blank control were determined by scanning electron microscopy (SEM) with energy dispersive X-Ray (EDX) spectroscopy (Quanta FEG250 scanning electron microscope).

The X-ray photoelectron spectroscopy (XPS) spectra of the roots after sorption were obtained by an ESCALAB MK II spectrometer (VG Instrument Group LTD., UK) using Mg K radiation ($E = 1253.6$ eV). The XPS peak intensity was recorded as counts per second (CPS). XPS Peak 4.1 was employed to deconvolve the N1s and O1s peaks using the Shirley baseline and an iterative least-squares fitting algorithm with a Lorentzian - Gaussian sum function (Zhang et al., 2006).

3. Results

3.1. Competitive sorption performances of Cu(II) and Cd(II)

Sorption of metal species by the water hyacinth roots was affected by each other. Fig. 1a shows the equilibrium sorption amounts of Cu(II) in the presence of various amounts of Cd(II). With

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