The Simultaneous and Synergistic Sorption of Phenanthrene and Cadmium Using Biomass Derived from Rice Roots

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Evaluating the sorption performance of coexisting phenanthrene and cadmium on rice roots is critical for a better understanding of plant sorption and uptake of combined pollutants. Batch sorption kinetics and isotherms of phenanthrene and cadmium on rice root biomass, as well as key factors in both single and binary systems, were evaluated to access any potential synergistic effects. Results showed that rice root biomass effectively and simultaneously removed phenanthrene and cadmium from aqueous solutions. The presence of a co-solute led to synergistic effects on the sorption, enhancing the affinity parameters, *i.e.*, the K_d (linear model), from 2530 to 3970 L/kg for phenanthrene, and the K_F (Freundlich model), from 640 to 777 L/kg for cadmium. The well fitted pseudo-second-order kinetics implied that the coexisting pollutants slowed the sorption rates, decreasing the sorption rate (k_2) from 0.185 to 0.155 g/mg/min for phenanthrene and from 0.0361 to 0.00146 g/mg/min for cadmium. The results suggested that further studies should carefully evaluate the remediation and risk-assessment in rice-arable soil under combined pollution.

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INTRODUCTION

Soil-related ecosystems, as subsystems of terrestrial ecosystems, are the most densely inhabited and biodiverse habitats on this planet and are important systems that humans rely on. Many important soil ecosystems, *e.g.*, farmlands and forests, function differently depending on the health of the soil and native biota. With human civilizations and development, numerous contaminants have been introduced into the environment, especially to the soil system (Premnath *et al*. 2021). Anthropogenic stress, primarily chemical pollution, impacts soil ecosystems and therefore jeopardizes their functions as well as the native biota (Höss *et al*. 2021). The contamination of various soil systems by heavy metals (including cadmium, arsenic, mercury, and chromium) adversely affects soil properties, microbial communities, and crop production (Shao *et al.* 2016). In addition, soil quality has become a global issue influencing human health and food security (Khan *et al*. 2021). In many cultivated regions, cadmium (Cd) is of concern due to its high concentration, high detection frequency, and high ecological risk (Khan *et al*. 2021).

Organic pollutants, including polycyclic aromatic hydrocarbons (PAHs) and halogenated organic pollutants, usually exhibit deleterious effects on soil biota and humans due to innate toxicity, *e.g.*, carcinogenicity, genotoxicity, cytotoxicity, mutagenicity, and neurotoxicity (Norén and Meironyté 2010; Bennett *et al*. 2021; Premnath *et al*. 2021).

As a complex absorbent, soil has the ability to retain various pollutants simultaneously and homogenously (Wolejko *et al*. 2020). Potentially toxic elements, *e.g.*, heavy metals, and hydrophobic organic compounds (HOCs), *e.g.*, PAHs, are widely found in the soil of contaminated sites as well as in farmlands (Shao *et al*. 2016; Zhao *et al*. 2021). The coexistence of these contaminants generally exhibits as combined risks rather than a simple summing of the individual effects. Many excellent studies focusing on low-concentration effects, combined toxicity, and toxic mechanisms have been published (Renner 2003; Kortenkamp 2007). In a complicated system, *e.g*., soil, the interactions between coexisting toxic chemicals and soil/soil biota can largely determine their environmental behaviors, fates, remediation strategy choices, and assessment implications. The effects of heavy metal-HOC interactions on sorption, as well as bio-transformations occurring on microalgae and bacterial/fungal surfaces, have been previously reported (Xiao *et al*. 2007; Tao *et al*. 2014; Chen *et al*. 2016). It seems that n-π electron-donor-acceptor interactions are supposed to be the dominant mechanism. However, additional studies are needed to better understand the interfacial process at various interfaces.

The responses of various soil organisms, *e.g.*, nematodes (Höss *et al*. 2021) and soil bacterial communities (Zhao *et al*. 2021), to combined chemical stresses have been tested. The combined presence of heavy metals in PAH-contaminated soil did not totally inhibit the potential for PAH degradation, but most heavy metals were negatively correlated with PAH degradation genes (Zhao *et al*. 2021). Nematodes responded differently to exposure concentrations of Zn and pyrene. Unfortunately, the coexistence effect of pyrene and Zn is still unclear and confusing (Höss *et al*. 2021). Furthermore, little information is available on the response of plants (roots), which is one of the most typical and abundant biotas in soil systems. Soil contaminants may sorb to roots and then be taken up, translocated, metabolized, or volatilized by the plant. Therefore, the sorption of contaminants to plant roots is considered the first and most important step for better understanding contaminant uptake, phytoremediation, and risk assessment (Dietz and Schnoor 2001). Even root properties may relate to plants competing with native/invasive congeners under chemical stress (Wang *et al*. 2021). Using sorption parameters, researchers have successfully estimated the root concentration factor, as well as the phytoremediation potential, based on sorption interactions among contaminants and plant roots/various components (Zhang and Zhu 2009; Torralba-Sanchez *et al*. 2017). However, under the combined chemical stress of heavy metals and HOCs, the sorption performance of plant roots is still unclear.

Therefore, the primary objectives of this study were to evaluate the sorption performance of heavy metal-HOC combination *via* rice root biomass from aqueous solutions using the following methods: (1) evaluation of the kinetics and isotherms of phenanthrene and Cd sorption using rice root biomass from aqueous solutions; and (2) assessment of the coexisting chemical interactions on the sorption performance.

EXPERIMENTAL

Chemicals

Phenanthrene (PHE) and Cd were selected as representative of HOCs and heavy metals, respectively, and were purchased from Aladdin Reagent Co. (Shanghai, China) with purities greater than 99.0% (without further purification). All other chemical reagents were of analytical reagent grade.

Rice Cultivation, Medium, and Root Biomass

Rice (*Oryza sativa* L.) seeds were disinfected using a hypochlorous acid solution before germinating on wet gauze and were incubated at a temperature of 25 °C in the dark. After 5 d, the seedlings were transferred and grown in black-covered glass beakers containing half-strength Hoagland solution in a greenhouse for 4 weeks. The half-strength Hoagland solution was composed of 945 mg/L of $Ca(NO_3)_2$, 506 mg/L of KNO_3, 80 mg/L of NH_4NO_3, 493 mg/L of $MgSO_4$, 136 mg/L of KH_2PO_4, 13.9 mg/L of $FeSO_4$, and 18.65 mg/L of EDTA-2Na (in distilled water).

Fresh roots in symmetrical plants were harvested from the greenhouse and immediately cut into approximately 5 mm pieces. The rice root biomass (RRB) was further prepared *via* cryodesiccation following mechanical grinding.

Sorption of Phenanthrene and Cd by Root Biomass in Single and Binary Systems

Batch sorption experiments were conducted to assess the sorption performance of RRB for PHE and Cd in an aqueous solution in both single and binary systems. Under kinetic and isotherm sorption conditions, a subsample of the RRB (0.01 g) was carefully weighed and transferred to 22 mL glass tube with 20 mL of solution containing either PHE alone, Cd alone, or a combination of both with 0.02 mol/L of $CaCl_2$. In the kinetic sorption, time schedules ranged from 0 to 24 h. In the isotherm sorption assay, the concentrations of PHE and Cd (in both the single and binary systems) ranged from 0 to 1.0 mg/L and from 0 to 100 mg/L, respectively. During the sorption process, the systems were kept stable at a temperature of 25 °C and stirred with a rotation rate of 150 rpm in a thermostated shaker. Samples with each treatment were prepared in duplicate. Control treatments containing pollutants but no RRB were also prepared in duplicate to account for possible loss by handling and volatilization. At each interval time or at equilibrium (based on kinetic experiments), the tubes were sampled and centrifuged for 15 min at 4000 *g*, and then the supernatants were filtered using 0.22 μm filter membranes (ANPEL Co., Ltd., Shanghai, China).

The RRB, before and after sorption under both single and binary conditions, was characterized using Fourier-transform infrared spectroscopy (FTIR) (Shimadzu 8400S, Kyoto, Japan).

Data Analytical Equations and Models

The removal efficiency and sorption amount of PHE and Cd by RRB were calculated based on the aqueous concentrations, according to Eqs. 1 and 2,

$$Removal\ efficiency\ (\%) = (1-C_i/C_t) \times 100\% \tag{1}$$

$$Q_t = (C_i-C_t) \times V/m \tag{2}$$

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where C_i and C_t (mg/L) are the concentrations of PHE and Cd at the initial time and at any sample time t, respectively, Q_t (mg/kg) is the sorption capacity of RRB for PHE and Cd, V (mL) is the volume of the solution and equaled 20 mL in the present study, and m (mg) is the mass of sorbents.

The pseudo-second-order kinetic model was used, and is generally expressed according to Eq. 3,

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{3}$$

where Q_e (mg/g) and Q_t (mg/g) are the sorbed PHE or Cd at the equilibrium time and time t, respectively, and k_2 is the pseudo-second-order rate constant (g/mg/min).

The isotherm data was fit by the Freundlich model ($Q_e = K_F \cdot C_e^n$) and a linear model ($Q_e = K_d \cdot C_e$). The linear form of the Freundlich model was used in this study as shown in Eq. 4,

$$logQ_e = logK_F + n^{-1}logC_e \tag{4}$$

where Q_e (mg/kg) and C_e (mg/L) are the sorption amounts for both solutes at the equilibrium time and equilibrium concentration, respectively, and K_F (L/kg) and K_d (L/kg) are the Freundlich constant and linear distribution coefficient, respectively.

Analytical Methods

The aqueous concentration of PHE in the samples was measured using high-performance liquid chromatography (HPLC) (Agilent 1260) equipped with a fluorescence detector and an Eclipse PAH column (4.6 mm $\times$ 250 mm). The mobile phase was composed of a methanol and water mixture (95 to 5 ratio, V:V) at a flow rate of 1.0 mL/min. The excitation and emission wavelengths for PHE were 244 and 360 nm, respectively. The limit of detection (LOT) and relative standard deviation (RSD) for PHE were 3.39 μg/L and 0.23%, respectively, as reported in a previous study by the authors (Zhang *et al*. 2018). The concentration of cadmium in the aqueous phase was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES) (Thermo iCAP6300). The LOT and RSD for Cd were 0.0196 μg/L and 0.39%, respectively.

RESULTS AND DISCUSSION

Characterization of rice root biomass (RRB)

The FTIR spectrum of the RRB used in this study confirmed that the biomass surface had abundant functional groups, including saturated aliphatic carbons and carboxyl, hydroxyl, aromatic, and ether structures (as shown in Fig. 1).
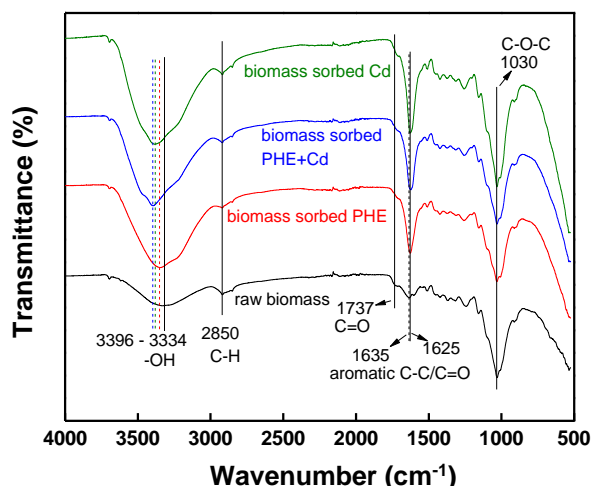
Fig. 1. FTIR spectrum of the RBB before and after the sorption of PHE and/or Cd

A strong vibration near 1030 cm^{-1} denoted an ether bond (C-O-C). The C=O at -COOH stretching was observed at approximately 1737 cm^{-1} (Mahmoud *et al*. 2017). Aromatic C-C and C=O asymmetric stretching vibrations were also found near 1625 cm^{-1}, which shifted to 1635 cm^{-1}, likely due to the presence of sorbed Cd and/or PHE (Zhang *et al*. 2013a). The series of peaks, ranging from 1182 to 1592 cm^{-1}, indicated saturated and unsaturated C-H. The band at 2850 cm^{-1} was dominated by saturated aliphatic groups, *e.g.*, C-H. The slight shifts of the peaks near 3334 to 3396 cm^{-1} might contribute to the sorption of Cd by RRB through the hydrogen bond interaction of heavy metal with –OH.

Sorption performance of rice root biomass (RRB) in single and binary systems

The sorption kinetics of PHE and Cd in an aqueous solution by RRB were determined and are illustrated in Fig. 2. As shown in Fig. 2A, a typical biphasic sorption model was exhibited for all conditions (for both PHE and Cd, and for both single and binary sorption). This phenomenon has been extensively discussed, with an initial dramatic increase in the sorption capacity (*Q*), followed by a steady plateau (as shown in Fig. 2A), and is generally proposed to saturate the available sorption sites (Fanaie *et al*. 2017; Zhang *et al*. 2018). For all conditions, sorption equilibrations were achieved in less than 480 min.
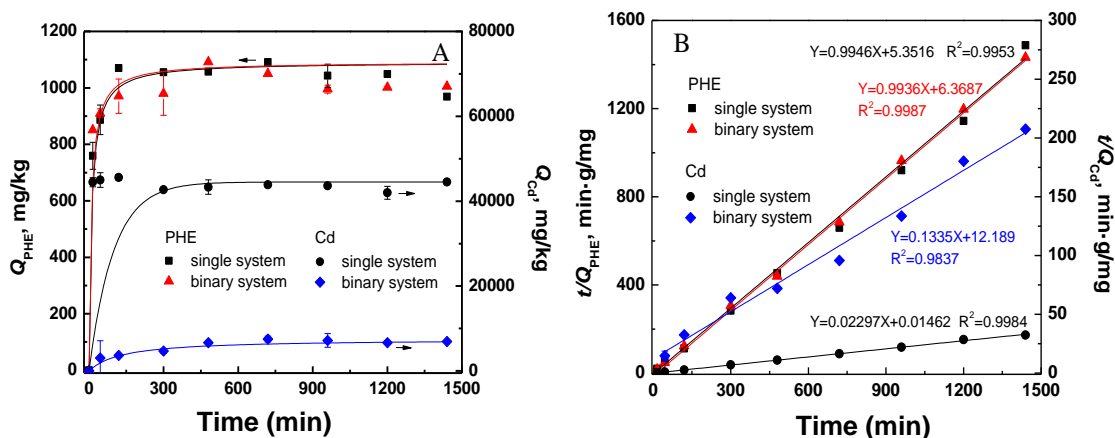

Fig. 2. Sorption kinetics of PHE and Cd by RRB in single and binary systems (A); and simulation using a pseudo-second order model (B)

The maximal sorption capacities for PHE by RRB were approximately 1091 and 1092 mg/kg, respectively, almost the same values in the absence and presence of cadmium. However, the presence of PHE considerably affected the maximal sorption capacity for Cd, which decreased from 45,590 mg/kg to only 7,510.0 mg/kg. The sorption capacity of Cd by RRB was relatively higher or comparative to that of previous reported. For example, the maximal sorption capacities of Cd on wheat straw- and swine manure-derived biochars ranged from 1960 to 52450 mg/kg (Xu *et al*. 2014). Eeshwarasinghe *et al.* (2019) also reported that the combined presence of PHE and acenaphthene considerably reduced the sorption of Cd by granular activated carbon. The sorption of HOCs, *e.g.*, PHE, by biomass is primarily due to hydrophobic interactions, *e.g.*, partitioning with aliphatic and aromatic structures (aromatic C-C, C=O at 1625 cm^{-1} and saturated C-H at 2850 cm^{-1}, as shown in Fig. 1) (Zhang *et al*. 2018). The interaction of heavy metal cations, *e.g.*, Cd^{2+}, with biological components typically contributes to surface functional groups, *e.g.*, hydroxyl and carboxyl groups (-COOH at 1737 cm^{-1} and -OH at 3334 cm^{-1}, as shown in Fig. 1) (Nicomel *et al*. 2021). The sorbed coexisting cadmium on the surface groups of the RRB provided extra sorption sites for PHE through *n-π* interactions, resulting in synergistic sorption for PHE (Xiao *et al*. 2007). However, the sorption of coexisting PHE occurred primarily by partitioning, which made it difficult to offer extra sorption sites for Cd, resulting in no additional sorption of Cd compared to the single system.

To further assess the diffusion mechanism and sorption rate of PHE and Cd by single and binary systems, a pseudo-second-order model (as shown in Eq. 3) was applied to fit the dynamic data, which fit superbly (as illustrated in Fig. 2 and Table 1). The theoretical sorption capacities (Q_e) calculated from the pseudo-second-order model were 1.005 and 1.006 mg/g for PHE and 43.5 and 7.49 mg/g for Cd in the single and binary systems, respectively, which agreed fairly well with the experimental data. The sorption rates (k_2) and calculated initial sorption rate h (mg/g/min, equal to $k_2Q_e^2$) of PHE and Cd by RRB were compared in the single and binary systems (Table 1). The results indicated that the presence of co-contaminants slowed the sorption rate.

Table 1. Kinetic Constants for Phenanthrene (PHE) and Cd in Single and Binary Systems Using Rice Root Biomass (RRB) as a Biosorbent

	k_2 (g/mg/min)	Q_e (mg/g)	h (mg/g/min)	R^2
PHE (single)	0.1848	1.0054	0.18686	0.9953
PHE (binary)	0.1550	1.0064	0.15702	0.9987
Cd (single)	0.03609	43.535	68.399	0.9984
Cd (binary)	0.001460	7.4906	0.082041	0.9837

Isotherm sorption experiments of PHE and Cd by RRB in single and binary systems were conducted, and a linear model and Freundlich model were applied (Fig. 3). The sorption isotherms were linear, and the regression constants, *i.e.*, R^2, (Table 2) indicated that the linear model fit best. The distribution coefficient (K_d) is considered a good constant for evaluating the sorption affinity of pollutants by (bio)sorbents. The K_d values for PHE and Cd under both single and binary conditions were calculated and are listed in Table 2. Previous studies have shown that biomass from bacteria, fungi, and algae could effectively sorb HOCs, *e.g.*, PAHs, organic chlorinated pesticide, and polychlorinated biphenyls, *via* a partition mechanism (Chen *et al*. 2010; Xu *et al*. 2016). In the present study, the presence of abundant aromatic (C-C, C=O at 1625 cm^{-1}) and saturated aliphatic (C-H at 2850 cm^{-1})

structures in the RRB provided effective sorption sites for PHE. The K_d values of PHE in both the single and binary systems (2530 and 3970 L/kg, respectively) indicated RRB had a high affinity for PHE. The log K_d values determined for PHE by RRB in single and binary systems were 3.40 and 3.60, respectively. These values were comparable to those reported for plant-derived biomass, including plant roots, leaves, and peels, which ranged from 3.20 to 3.84 (Chen *et al*. 2011; Chen *et al*. 2018). The sorption affinity of PHE by RRB was much greater than that of typical soil (a log K_d of 1.48 to 2.30) and comparable with that of microbiological biomass (a log K_d of 2.98 to 3.89), as summarized in the previous work by the authors. This indicated that RRB could play an essential role in the transport and fate of PHE in soils and surface water (Zhang *et al*. 2018). Furthermore, the presence of coexisting Cd considerably enhanced the sorption affinity of PHE, with an increase of 56.7% in the K_d of PHE. Under binary conditions, RRB-sorbed Cd neutralized the RRB surface through complexation with deprotonated functional groups, *e.g.*, carboxyl groups (as illustrated *via* FTIR in Fig. 1). The increased hydrophobicity of the RRB provided more partition regions for the extra sorption of PHE *via* hydrophobic effects. In addition, PHE is usually recognized as a π-donor (Xiao *et al*. 2007). As such, the π H-bonding of PHE with protonated carboxyl groups (due to sorbed Cd) may also occur.

For Cd, sorption by biomass occurs through complexation with surface functional groups, *e.g.*, carboxyl and hydroxyl groups. It is widely believed that functional groups complexation is a major mechanism for biomass and biomass-derived materials to sorb heavy metal cations, *e.g.*, Pb^{2+}, Cd^{2+} (Zhang *et al*. 2013). Although the coefficient of determination (R^2) of the Freundlich model was not as good as that of the linear model, simulation with the Freundlich model was still found to be acceptable. In the presence of co-contaminant PHE, the K_F of Cd increased by 21.6%, from 639 to 777 L/kg (in Fig. 3B and Table 2). The influence of the presence of a co-solute was not equivalent for PHE and Cd. There are probably two reasons for this: (1) the concentration of PHE was much lower than that of Cd, resulting in a limiting effect on Cd sorption; and (2) the coexisting PHE partitioned to aromatic and aliphatic moieties and had little impact on the complexation functional groups in the RRB surface for Cd sorption.
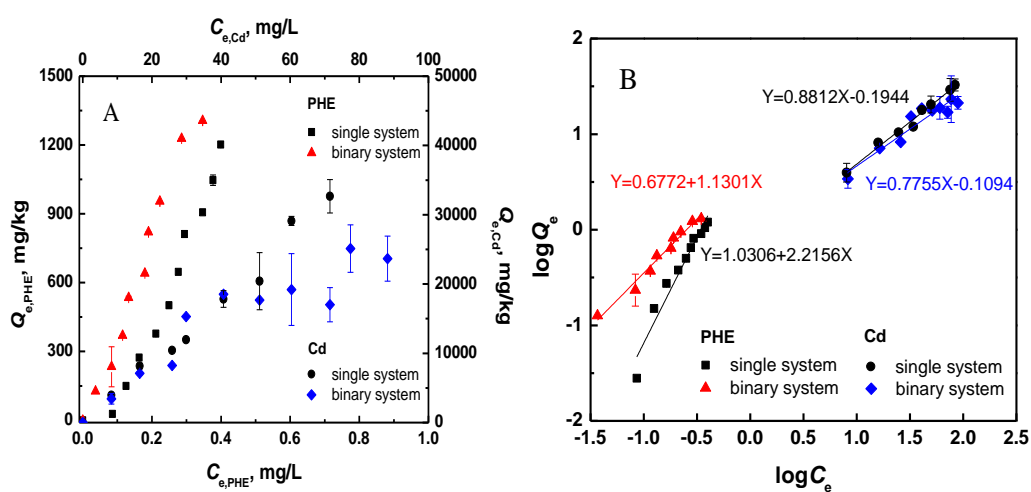

Fig. 3. Isothermal sorption of PHE and Cd by RRB in single and binary systems (A); and simulation using the Freundlich model (B)

Table 2. Isotherm Sorption Constants for Phenanthrene (PHE) and Cd by Rice Root Biomass (RRB) in Single and Binary Systems

	Linear model		Freundlich model		
	K_d, L/kg	R^2	K_F, L/kg	n	R^2
PHE (single)	2532.6±155.43	0.9601	10730	0.4513	0.9436
PHE (binary)	3968.7±118.92	0.9911	4755.5	0.8849	0.9733
Cd (single)	445.798±11.198	0.9944	639.15	1.1348	0.9833
Cd (binary)	309.396±20.498	0.9538	777.32	1.2895	0.8968

Effects of pH and ionic strength on the sorption performance

  Generally, the pH of an aqueous or soil solution is considered to be one of the most important factors determining sorption behavior. As expected, the sorption capacity for PHE remained relatively stable (1230 to 1580 mg/kg in single and 1320 to 1780 mg/kg in binary systems) under a relatively wide range of pH (3 to 7), and no significant differences were observed (Fig. 4A). As mentioned above, partitioning was the dominant mechanism proposed for the sorption of PHE by RRB, and partitioning seemed to be insensitive to changes in pH (Zhang *et al.* 2018). However, the changing pH strongly affected the sorption capacity for Cd (Fig. 4A). When the solution pH increased from 3 to 7, the sorption capacity increased from 3800 to 30140 mg/kg in the single system and from 2460 to 11630 mg/kg in the binary system. Similarly, the presence of PHE diminished the sorption capacity of Cd at all test pH values. Even so, the presence of PHE alleviated the influence of pH on Cd sorption. At lower pH (*e.g.*, 3 or 4), the strong acidic environment caused the protonation of surface anionic functional groups such as carboxyl groups of RRB and weakened its binding ability with Cd.
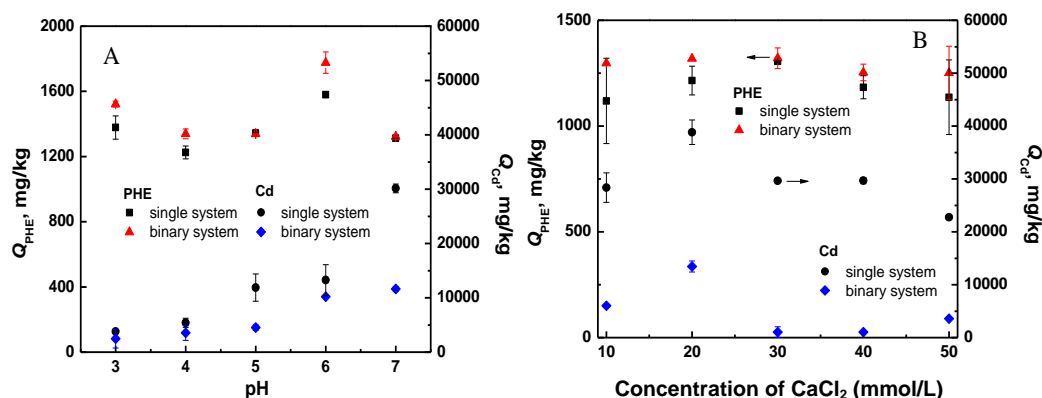
Fig. 4. Effects of solution pH (A) and ionic strength (B) on the sorption of PHE and Cd by RRB

  Ionic strength, as an important water chemistry factor, plays a considerable role in sorption, especially in metallic bonds. The effects of ionic strength on the sorption capacity of RRB for PHE and Cd in single and binary conditions were investigated. As shown in Fig. 4B, the sorption of Cd was remarkably affected. With increasing concentrations of CaCl2, the sorption capacity of Cd on RRB initially increased and then decreased from 28,400 mg/kg at 10 mmol/L CaCl2 to 22,800 mg/kg at 50 mmol/L CaCl2. These results were consistent with previous reports (Mahmound *et al.* 2017), speculating the competition of Ca^{2+} as a major contributor. However, no obvious difference in the sorption of PHE was observed under various CaCl2 concentrations, as shown in Fig. 4B. In accordance with the results described above, the presence of Cd enhanced the sorption capacity of phenanthrene at all CaCl2 concentrations tested in this study.

CONCLUSIONS

1. The biomass derived from rice roots can effectively and simultaneously remove phenanthrene and cadmium from aqueous solutions, with strong affinities (3970 L/kg linear K_d for phenanthrene and 778 L/kg Freundlich K_F for cadmium, respectively).

2. Synergistic effects were implied under binary conditions, enhancing the K_d by 56.7% for phenanthrene by the presence of cadmium, and the K_F by 21.6% for cadmium by the co-existing phenanthrene. The coexisting cadmium interacted through complexation with deprotonated functional groups, *e.g.*, carboxyl groups, of the RRB, increasing the hydrophobicity of the RRB surface, thereby enhancing the extra sorption of phenanthrene.

3. Coexisting pollutants slowed the sorption process, where the calculated pseudo-second-order sorption rate (k_2) decreased from 0.185 to 0.1550 g/mg/min for phenanthrene and from 0.0361 g/mg/min to 0.00146 g/mg/min for cadmium.

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