Abstract

Through sampling reed in Shuangtai estuary wetland in April, 2009 and simulation test in Shenyang Agricultural University, we analyze the removal efficiency of Cu, Zn, Pb and Cd during different growth period of reed and distribution of them in various parts of reed. The results show that the removal efficiency is best in jointing stage, the removal of Pb largest with 21% increase and 30% in sprout and exhibition leaf period, the removal of Zn largest with 53% and 29% increase in jointing stage and the maturity period, the removal of Cd largest with 40% increase in the different growing season. The absorption amount of Cu, Zn, Pb and Cd in roots of reed reaches maximum during the growth, followed by in stems and in leaves. Absorptive capacity in the whole plant for Cu, Zn, Pb and Cd exists extremely significant difference (p<0.01). The order is Pb>Zn>Cu>Cd. The absorption in root is higher than in stems and in leaves (p<0.05), but Zn and Cd absorption amount has no significant differences in stems and leaves (p>0.05).

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I . Introduction

With the rapid development of our national economy, water environment in China is facing grim challenge. Heavy metal pollution of water is extremely serious as the development of urbanization and industrialization in recent years[1]. Because copper, zinc, lead and cadmium are the main index for water environment quality evaluation standards[2]. When they accumulated to a certain extent, they not only damage ecological to cause soil degradation, crop yields and quality decreased, but also they enter the food chain and endanger human life and health[3]. So the task of purification of heavy metals in water is imperative.

Reed (Phragmites australis) belongs to gramineous perennial herbaceous plants and advantage plant variety in many aquatic ecosystems. Reed root hole on the ability of sewage treatment[4]can be used as materials that restore damaged riparian ecosystem[5]and it has certain absorption and cumulative effect
for heavy metal pollutants[6]. In recent years, many foreign scholars have widely studied on toxic heavy metals absorption and distribution in wetland reed. Researchers such as Weis[7], Windham[8], analyzed and compared distribution of toxic heavy metals and absorbency in reed, Aksoy[9] discussed the rules of migration and release of toxic heavy metals in reed. Whereas our nation has done more research on absorption and purification of heavy metal by mangrove plants than reed. These mangrove plants mainly include Avicennia marina[10], Kandelia candel[11] and Aegiceras corniculatum[12]. Shuangtai estuary wetland is the final barrier of Shuangtai into Bohai Sea. Water quality of Liaohai river has deteriorated, and its heavy metal content has exceeded national surface water standards.[13] Research on the reduction of copper(Cu), zinc(Zn), lead(Pb) and cadmium(Cd) in paper-making wastewater by Shuangtai estuary wetland reed has been rare reported. This research establishes a small system device which simulates Shuangtai estuary wetland naturally. It mainly researches the purification effect of four heavy metals by wetland reed in the different growth periods and parts. Furthermore, it provides the theoretic basis and the technical support and analyzes the mechanism of wetland reed purifying heavy metal in water.

1.1. Experimental section

*Experimental wastewater.* Experimental wastewater was sampled from the sewage outfall of Jincheng Paper Mill. Ten buckets were transferred to the test ground at Shenyang Agricultural University on the first day of each month. They were used to irrigate the experimental basin on the fourth day of the month. Sampling time is from April through November. Papermaking wastewater quality condition is in Table 1.

| main ingredients | COD (mg/L) | BOD₅ | copper | zinc | lead | cadmium | volatile phenol | SS | salinity | PH |
|------------------|-----------|-------|--------|------|------|---------|----------------|----|----------|----|
| content (mg/L)   | 1610      | 823   | 0.05   | 0.07 | 0.08 | 0.003   | 0.05           | 141| 3569     | 7.87|

*Experimental soil.* Natural soil from Shuangtai estuary wetland was used to transplant reeds in experimental area. The soil has thawed in April 2009. This is a meadow soil with the pH 8.47, organic matter 1.12% and bulk density 1.03 g/cm³.

*Experimental plants.* Reeds are sampled from the natural estuarine wetland reserve of Shuangtai in Panjin City. The reeds were local species, such as Liaobin reed and Panjin reed, and naturally mixed planting. Healthy reed roots were dug out during germination in April 2009. They were cut into small sections (30 cm), and sheared, bagged and sprayed with water. Then, they were transplanted into test pools of Shenyang Agriculture University.

*Experimental arrangement.* Each experimental unit is 1 m × 2 m, and its basic buried depth 0.8 m, the height of the aerial part 0.9 m and the inner depth 0.8 m (Figure.1). Four outlet pipes are installed in the side of each experimental pool at an interval of 10 cm. Soil from Shuangtai estuary wetland is transferred to a depth of 20 cm in each pool. Then, reed roots are transplanted into each pool with a spacing of 0.04 m × 0.04 m. The actual growing state of reed roots is shown in Figure 1.

Based on the standard of growing periods devised by Irrigation Experiment Standard, the reed plant growing seasons are divided into germination period, leaf extension period, jointing period, heading to flowering and mature period. According to these growth periods, five experimental basins are designated respectively as I , II, III, IV, V . Then 100% concentration of paper-making wastewater irrigates the pools during the different growth periods.

At the beginning of growth period, the 100% concentration of wastewater pours into pools water depth in 10cm. Only irrigate clean water to prevent Cu, Zn, Pb, Cd accumulation from affecting growth during growth periods. The day before next growth period when pouring papermaking wastewater, we have taken the water samples and plant samples.
Sample collection and pretreatment. Water samples are layered collected through the four lateral pipes and then filtered and refrigerated. Sample three well-growing strains in each pool and divide them into root, stem and leaf to be tested after processing and decomposition[14]. Four kinds of heavy metals (Cu, Zn, Pb and Cd) content of water and plants are tested by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and analyzed by statistical software (SPSS 17.0).

Instruments and reagents. The inductive coupling plasma emission spectrograph is from the US Thermal Power Company. The reagents are obtained as follows: multi-element standard solutions containing 56 species of metals (national standard sample from National Standard Material Net), concentrated H₂SO₄, concentrated HNO₃ and concentrated HClO₄ (Shenyang National Medicine Group).

1.2. Results and analysis

Purification effect of reed to Cu, Zn Pb and Cd in papermaking wastewater in different growth periods. Draw curve of reed removal rate to Cu, Zn, Pb and Cd in different growth periods. It reflects reed purification effect in papermaking wastewater clearly. (Figure 2)
Generally speaking, removal rate of reed has the same trend in different growth periods. Removal rate to four heavy metals is the highest at jointing stage, removal rate lowest at sprout period. Removal rate is similar at exhibition leaf period, heading and maturity stage.

Removal rate to Cu at jointing stage is the largest at 30%, and followed by heading and exhibition leaf period 24% and 22%, respectively. Removal rate to Cu at sprout period and maturity is the least 19% and 18%. Through analysis of variance of reed removal rate to Cu in different growth periods (Table 2), the results show p value 0.037 < α = 0.05, so reject the null hypothesis H₀. Reed removal rate to Cu in different growth period has remarkable influence. Removal rate to Zn has a mark peak (53%) at jointing stage, removal rate to Cu 37% and 29% at heading and maturity stage, exhibition leaf stage and sprout stage is lower 19% and 13% respectively. Through analysis of variance of reed removal rate to Zn in different growth periods (Table 3), the results show p value 0.009 < α = 0.01, so reject the null hypothesis H₀. Reed removal rate to Zn in different growth period has remarkable influence. Reed removal rate to Pb at jointing stage is the highest 50%, then removal rate at heading exhibition leaf and ripe stage are 33%, 30% and 23%, respectively. Reed removal rate at sprout period is the least 21%. Through analysis of variance of reed removal to Pb in different growth periods (Table 4), the results show that inspection p value 0.008 < α = 0.01, so reject the null hypothesis H₀. Reed removal to Pb in different growth period has remarkable influence. Reed removal rate change in trend to Cd is exactly the same as Pb. Through analysis of variance of reed removal rate to Cd in different growth periods (Table 5), the results show inspection p value 0.028 < α = 0.05, so reject the null hypothesis H₀.

Because reed absorptive capacity to heavy metal in different growth period is different, reed removal rate to Pb are both reached the maximum in sprout period and exhibition leaf period. Secondly, reed removal rate to Cd, Cu and Zn reaches the minimum. In reed jointing stage, reed removal rate to Zn is the largest 53%, followed by Pb 50%, Cd and Pb 46%, Cu 30%. In reed irrigation, reed removal rate to Cd, Zn and Pb are similar 40%, 37% and 33%, respectively. Reed removal to Cu is the least 24%. In reed maturity period, reed removal rates to four different heavy metals are Zn 29%, Cd 25%, Pb 23%, Cu 19% in descending order. The reason for reed removal rate different to heavy metals at different growth is that

| Variation source | Sum of Squares | df | Mean Square | F value | P value |
|------------------|----------------|----|-------------|---------|---------|
| **Between Groups** | 9.980          | 4  | 2.470       | 1.87    | 0.009** |
| **Within Groups** | 5.133          | 12 |             |         |         |
| **Total**        | 15.133         | 16 |             |         |         |

| Variation source | Sum of Squares | df | Mean Square | F value | P value |
|------------------|----------------|----|-------------|---------|---------|
| **Between Groups** | 5.290          | 4  | 1.320       | 3.03    | 0.008** |
| **Within Groups** | 1.989          | 12 |             |         |         |
| **Total**        | 7.279          | 16 |             |         |         |

| Variation source | Sum of Squares | df | Mean Square | F value | P value |
|------------------|----------------|----|-------------|---------|---------|
| **Between Groups** | 4.872          | 4  | 1.210       | 4.12    | 0.028*  |
| **Within Groups** | 2.963          | 12 |             |         |         |
| **Total**        | 7.835          | 16 |             |         |         |
each factor in wetland system is interactional in heavy metal removal process. Different factor combination has different effect on existing state of heavy metal elements[1]. The mechanism of competition between different heavy metals remains further study.

**Purification effect of reed to Cu, Zn ,Pb and Cd in different parts.** Through analysis of the distribution of Cu, Zn, Pb, Cd in different parts in root, we can more clearly understand the effect of purifying heavy metals in each part. Specific distribution and accumulation is shown in Figure 3. Results: Distribution of four heavy metals has a certain regularity. Absorption of heavy metal in different parts was arranged in order, root> stem> leaves. The reason for rule of most plants is that root endothelium could keep from heavy metal transporting to the ground. Romheld[15] argued that grass roots organization can secrete a kind of iron-deficiency secretions - megan acids (phytosiderophores), which not only activate hard dissolved Fe element in the sediment, but also activate Cu, Zn, Cd, Pb and other metal elements. In order to promote absorptive capacity of the root tissue, Zhu H M, and others have studied absorption characteristics of Tidal flat wing alkali peng to heavy metals. They also got similar results[16].

### Table 6 distribution characteristics of heavy metals at different parts of the reed

| parts         | absorption of Cu (mg/L) | absorption of Zn (mg/L) | absorption of Pb (mg/L) | absorption of Cd (mg/L) |
|--------------|-------------------------|-------------------------|-------------------------|-------------------------|
| root         | 0.0340±0.0080a          | 0.0670±0.0120a          | 0.0800±0.011a           | 0.0032±0.0010a          |
| stem         | 0.0150±0.0030b          | 0.0260±0.0050c          | 0.0310±0.009b           | 0.0015±0.0003c          |
| leaves       | 0.0070±0.0010ab         | 0.0110±0.0020bc         | 0.0110±0.004c           | 0.0007±0.0001bc         |
| the whole plant | 0.0560±0.0120**         | 0.1040±0.0190          | 0.1220±0.024           | 0.0054±0.0014           |

**Fig.3** distribution of four kinds of heavy metals (Cu, Zn, Pb, Cd) at different parts of the reed

Distribution feature of heavy metals in different parts of reed is shown in Table 6. Absorptive capacity of the whole plant to Cu, Zn, Pb and Cd has extremely significant difference (p < 0.01). The order of uptake is Pb>Zn>Cu>Cd. The uptake of heavy metals in different parts of reed has obvious difference. Uptake of Cu, Zn, Pb, Cd in root is respectively significant higher than in stems and leaves (p < 0.05). Uptake Zn and Cd in stems and leaves has no significant difference (p > 0.05). This shows that root has the effect of Cu, Zn, Pb, Cd enrichment. Wetland reed of Shuangtai river absorbs heavy metal elements and stores them in the root. Reed can reduce the second pollution by falling leaves and the possibility of heavy metals traveling along the food chain, and thus has a purify environment effect.

### Discussion

This study only considers one kind of wetland plants for the purification of heavy metals from paper-making wastewater. But in practice a combination of a variety of plants may be needed to purify complex pollution which may contain a range of heavy metals. Whether there is synergy or antagonism between heavy metals removal processes, it remains further study.

In conclusion, our results indicate that the reed roots play an important role in removal of heavy metals in wetland, but differences of root in structure may also affect reaction process. For example, thick roots and rootlets, deep roots and shallow roots may have different capacities for the absorption and accumulation of heavy metals in their vicinity. This aspect is also worthy of further investigation.
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