

# Removal of Complex Heavy Metals from Agricultural Waters Using Artificial Wetlands

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**Abstract** In order to solve the environmental problems of compound heavy metal pollution in farmland water, a vertical submersible artificial wetland wastewater treatment simulation device was established using different forms of substrate configuration to remediate heavy metal pollution in farmland water. Four groups of artificial wetland systems were constructed in the greenhouse with the substrates of gravel, zeolite, biochar and zeolite-biochar, and the changes of effluent water quality and the effects of nitrogen and phosphorus removal were observed to investigate the long-term treatment effects of different substrates on the wastewater containing composite heavy metals, and the distribution characteristics of the heavy metals in the artificial wetland. The removal rate of each heavy metal by each group of artificial wetland was calculated, and the flux of  $Cd$  retention in the wetland system was further analyzed to describe the role of plants in the artificial wetland. The results showed that the effluent from all the devices was in a low dissolved oxygen state, and the pH value gradually decreased. The combined removal rate of heavy metals in wastewater by each group of artificial wetland systems reached more than 70% overall, but the combined removal rates of different heavy metals were different.

**Index Terms** heavy metal removal, heavy metal pollution,  $Cd$  retention flux, artificial wetland, effluent water quality

## I. Introduction

There are three main sources of heavy metal pollution in farmland, namely, fertilizer input, atmospheric input and water input, and the persistent heavy metal pollution input will have a negative impact on the long-term healthy development of agriculture and the security of agricultural supply through chain reaction [1]-[3]. At present, one of the main factors of water pollution in China's farmland irrigation is heavy metal pollution, heavy metal pollution of water bodies in the irrigation of farmland so that the crops in the farmland are contaminated, and the safety of the residents' diet is not guaranteed, which has a huge impact on the health of the residents [4]-[5]. Heavy metal pollution compared to other pollutants has irreversible, long-term and hidden characteristics, and in the natural environment, heavy metals can not be directly decomposed to remove, will exist in the natural environment for a long time [6]-[8]. When the heavy metals in the water body exceeds a certain concentration, the organisms in the water body will also ingest the heavy metals, the phenomenon of bioconcentration, suffer from the toxicity of heavy metal pollution, cause the heavy metal content in the plants to be too high, and through the trophic level of the biological chain transfer to the human body, so as to make the human body's health and safety is threatened [9]-[12]. Therefore, purification of heavy metal pollution in farm irrigation water, restoration of water bodies and improvement of water quality is one of the environmental problems that need to be solved urgently in China.

Artificial wetland is an artificial simulation of natural wetland, which is often applied in wastewater treatment because of its good biogeochemical cycle function [13]. Numerous studies have shown that artificial wetlands can effectively remove heavy metal mass fractions from wastewater such as domestic water, mining effluent and industrial wastewater, and they are equally effective in treating agricultural irrigation water [14]-[16]. Due to the low construction cost, low operational energy consumption, and easy operation and management of artificial wetlands, they are widely used at home and abroad [17].

In this paper, we determined the sampling methods and abatement methods of water samples, plants and soils, converted the integrated effect value to integrated removal rate, and utilized the integrated removal rate to illustrate the effect of the artificial wetland system on the removal of heavy metals in wastewater. By filling different heavy metal adsorption materials, four groups of artificial wetlands, CK, F, S and FS, were set up, embodied as four groups of vertical submerged artificial wetland sewage treatment simulation devices with different proportions of gravel, zeolite and biochar. Compare the changes in effluent water quality and the effect of nitrogen and phosphorus

removal of artificial wetland systems with different substrate configurations, and calculate the average removal rate of effluent water quality indicators. Further analyze the comprehensive removal rate of  $Cr$ ,  $Cd$ ,  $Cu$ ,  $Pb$  and  $Zn$  by the artificial wetland systems with different substrate configurations. Observe the distribution of heavy metals in the artificial wetland in two observation points, above and below ground. Discuss the role of plants in the artificial wetland system.

## II. Basics of experimental design

### II. A. Heavy metal pollution

Heavy metals are one of the common pollutants in the environment that do not break down easily in the environment and can persist in the environment. For living organisms, heavy metals do not decompose in the body and can be enriched through the food chain. For the end of the food chain has serious damage, especially for humans there is a huge health risk [18], [19].

Cadmium is a non-essential element for plant growth and development, and its chemical symbol is  $Cd$ . When it exists in the form of  $Cd^{2+}$ , it is easily absorbed and accumulated by plants, thus causing harm to their vital activities.

Cadmium is harmful to plants mainly in the following aspects:

- (1) High concentration of cadmium stress inhibit plant seed germination.
- (2) High cadmium stress inhibits photosynthesis.
- (3) Cadmium stress affects plant protection enzyme activity.

The chemical symbol for zinc is  $Zn$ , and the main sources of soil zinc pollution are the three wastes (exhaust gas, waste water and slag) emitted from lead-zinc smelters, lead-zinc mines and electroplating industries. For plants, excess zinc inhibits chlorophyll synthesis and affects plant growth.

As a widely distributed element in nature, lead, whose chemical symbol is  $Pb$ , is mainly used in the production of batteries, as well as in the construction industry and, to a lesser extent, in other industries. When lead ore is used for production, lead-rich soot escapes when it is heated, and less than one-fourth of the large amount of lead that is consumed can be recycled, and the lead that is not recycled enters the atmosphere, slag, soil, and water bodies, causing widespread pollution and harming the environment. Lead affects the absorption and accumulation properties of plants, mainly in reducing the chlorophyll content of plants, which in turn affects the photosynthesis and respiration of plants, slowing down their growth.

The chemical symbol for copper is  $Cu$ , and copper pollution is mainly caused by dust, wastewater and slag produced during smelting, mining, metal processing and other human activities. At present, the effects of copper pollution in water and soil are mainly on animals and plants. Excessive copper in water can kill aquatic organisms and affect the growth of plants at the same time.

### II. B. Artificial wetlands

Artificial wetland is an ecological technology for wastewater treatment that is constructed artificially and by simulating the principle of natural wetland water purification, the main body consists of substrate, plants and microorganisms, which is to remove all kinds of pollutants in water through the synergistic effect of physical, chemical and biological [20], [21].

The basic composition of artificial wetland:

(1) Substrate, as a filler, is the main structure of the artificial wetland, and it is the plants that treat the pollutants. There are many types of substrates, commonly used are soil, gravel, zeolite, slag and other natural materials. In recent years, there are also many new modified materials as substrate.

(2) Plants, also an important part of artificial wetlands. Aquatic plants in wetlands can be divided into four major categories: aquatic plants such as reeds, iris and cattails, floating leaf plants such as water turtle, water lilies and Nymphaea, floating plants such as locust leaf pimpernel, Mannheimer's red and phoebe's lotus, and submerged plants such as goldfish algae, foxtail algae and bitter grass.

Aquatic plants have well-developed root tissues, which can effectively absorb and utilize the nitrogen and phosphorus in the sewage as nutrients for their own growth, and also photosynthesize to produce oxygen for the use of organisms in the wetland system, and can provide attachment sites and a suitable environment for various types of microorganisms to live in.

(3) Microorganisms are the most important part of the artificial wetland to remove pollutants, and the diversity of microorganisms varies according to the water intake, plants, substrate, etc. Bacteria and fungi are the most common, with the largest number of bacteria, which often act as "catalysts" in the artificial wetland, and the contribution of their denitrification can be up to 60%-70%.

## II. C. Removal of heavy metals by artificial wetlands

Removal of heavy metals from artificial wetlands is mainly through physical precipitation, filtration, chemical precipitation, adsorption, microbial interaction and uptake by plants. The uptake and bioconcentration of plants in artificial wetlands, the adsorption and precipitation of fillers, and the formation of sulfide precipitation from metal ions and  $S^{2-}$  are the main ways to remove heavy metals.

(1) Removal action of matrix. Physical adsorption and chemical action are the main ways to realize the removal of heavy metals by matrix. After entering the wetland, heavy metals undergo a series of physical and chemical reactions. In horizontal submerged flow or vertical submerged flow type artificial wetland, heavy metals are retained in the filler by chemical reaction with the filler, and finally absorbed by the artificial wetland plants or removed when the filler is replaced.

In addition, the artificial wetland substrate can enhance the removal of heavy metals into forms that are difficult to migrate and transform. Under anaerobic environment, sulfate is converted to  $S^{2-}$  under the action of microorganisms, thus making heavy metals precipitate into more stable sulfide.

(2) Removal effect of plants. Artificial wetland plants mainly remove heavy metals by adsorption, volatilization and absorption. In general, the uptake of metal ions by plants is very small. The removal of heavy metals by plants mainly regulates the distribution of trace metals in the solid and liquid phases. It can be divided into two processes: rapid adsorption on the plant surface and slow deposition and transport in the biomass.

Wetland plants transfer oxygen from the air to their roots, creating an aerobic zone within a certain range, where a portion of the oxygen diffuses outward, reoxidizing the originally deposited sulfides and releasing the heavy metals. Wetland plants can also release organic carbon to the surface of heavy metal precipitates to turn them into a reduced state. Thus, wetland plants enhance the cycling of sulfur and the transformation of metals between oxidized and reduced states. Wetland plants can also provide sites for microorganisms, and plant metabolites and residues and dissolved organic carbon provide food sources for sulfate-reducing bacteria and other bacteria in artificial wetlands.

(3) Role of microorganisms. Mainly include: ① Absorption or adsorption of heavy metals. ② The chelating and precipitating effect of microbial secretion protein on soluble heavy metals. ③ Indirect effect on the transformation of heavy metal form, sulfate-reducing bacteria in anaerobic conditions will be reduced to hydrogen sulfide sulfate, heavy metals and hydrogen sulfide reaction to generate precipitation and be removed.

## III. Materials and methods

### III. A. Experimental materials and apparatus

This paper was carried out in a greenhouse shed of a university's School of Resources and Environment, which was well ventilated and illuminated. The simulation device used a PVC drum with a bottom inner diameter of 35cm and a height of 40cm. The total height of the substrate filler in the drum was 30 cm (15 cm gravel at the bottom, 10 cm heavy metal adsorption layer in the middle and 7 cm gravel layer at the top).

Based on the different heavy metal adsorption materials filled, four groups of artificial wetlands were set up: the control group (CK) was 100% gravel. The zeolite group (F) was 40% zeolite + 60% gravel by volume. The biochar group (S) was 40% biochar + 60% gravel by volume. Zeolite-biochar group (FS) was 20% zeolite + 20% biochar + 60% gravel by volume ratio.

Two replicates were set for each treatment. Three PVC porous pipes of 30 cm length and 6 cm inner diameter were placed in the middle of the artificial wetland in each group for water intake, siphon drainage, water sample collection, and in situ index determination.

The gravel used in the experiment was ordinary architectural bluestone with a particle size of 1~3 cm, the zeolite was natural diagonal zeolite with a particle size of 1~3 cm, and the biochar was coconut shell biochar with a particle size of 0.8~1 cm.

Microorganisms were inoculated by the hanging film method, and activated sludge taken from the aeration tank of a wastewater treatment plant in the city was domesticated using artificially prepared effluent, with the influent pH set at  $7.31 \pm 0.042$ , dissolved oxygen at  $7.8 \pm 0.12 \text{ mg} \cdot \text{L}^{-1}$ , and hydraulic retention time of 1d, and then one-time inoculation was carried out to the experimental after stabilization of effluent. Device. The wetland plants were wild calamus, planted at a density of 30 plants  $\cdot \text{m}^{-2}$ , i.e., 4 plants per device.

### III. B. Experimental apparatus and reagents

The main reagents required for the experiment are shown in Table 1.

Table 1: The main reagent required for the experiment

Name	Company
Nitric acid	National drug collectivization co., LTD
Hydrochloric acid	Chemical testing products co., LTD
Reagent	National drug collectivization co., LTD
Cadmium standard solution	National drug collectivization co., LTD
Mixed standard solution( <i>Cr</i> , <i>Cd</i> , <i>Cu</i> , <i>Pb</i> , <i>Zn</i> )	National drug collectivization co., LTD

The experimental apparatus models are shown in Table 2.

Table 2: Experimental instrument model

Instrument name	Type	Company
Ultra pure water machine	ZWL-PAL-20	Water environmental protection technology co., LTD
Electronic balance	AUY220	Cyleis science instrument co., LTD
Intelligent solver	XJS36-42	Lepotley instrument company
Electric furnace	SW-1	Electric furnace factory
The number of air drying box	DHG-9076A	Shanghai jinghong experimental equipment co., LTD
Graphite furnace atomic absorption spectrometer	AA-240FS	Beijing gesky instrument company
ICP-MS inductance coupled plasma mass spectrum	8300	America, optima
High speed multi-function mill	AS-990F	Zhejiang industrial trading co., LTD

### III. C. Sampling methods

#### III. C. 1) Water sampling methods

Regular sampling of inlet and outlet waters in the pilot. Continuous monitoring was carried out in the farmland. The retrieved samples were processed immediately to determine and analyze the removal rate of heavy metals from different graded ponds, and calculate the remediation efficiency of the artificial wetland on heavy metal pollution. For the artificial wetland system, four sampling sites were set up, namely: No. 1 for the water inlet, No. 2 for pond 1, No. 3 for pond 2, and No. 4 for pond 3. Sampling was performed once every other week, and 500 mL of water samples were collected, collected in plastic bottles, and treated with nitric acid and then preserved in a refrigerator.

#### III. C. 2) Plant sampling methods

When collecting aquatic plants, care was taken to keep all parts of the plant intact, after collection, the substrate of each part of the plant was washed with tap water and then rinsed several times with ultrapure water, after rinsing, the parts were separated with scissors, packed in kraft paper bags, and put into the oven to keep it at 105°C for 1 hour, and then adjusted down to 70°C to bake until constant weight. After the plant samples were thoroughly dried, they were pulverized using a pulverizer, sieved, and stored in a sealed bag pending digestion.

#### III. C. 3) Soil sampling methods

Use a sampler to collect the substrate ten centimeters down from the surface of the bottom soil, mix and remove impurities such as plant roots, stones, etc., air-dry to no moisture, use a mortar and pestle to grind the soil samples to powder, sieve through a 100 mesh nylon sieve and then encapsulated to wait for the dissolution.

### III. D. Disinfection methods

#### III. D. 1) Plant digestion methods

1.0 g of plant samples were weighed separately and placed into an ablation tube, and 10 mL of HNO<sub>3</sub> solution was added to each ablation tube. The samples were placed on an ablation oven and the temperature was heated to 70 °C within 15 min and kept at 70 °C for 30 min, then the temperature of the oven was raised to 90 °C and kept at 90 °C for 30 min, and finally the temperature of the oven was raised to 120 °C and kept at 120 °C for 2 h. A curved-necked funnel was placed at the mouth of the tube to form a reflux flow throughout the ablation process. During the ablation process, a bent-neck funnel was placed at the mouth of the ablation tube throughout the process to form reflux. The reagents were diluted to 50 mL with ultrapure water and filtered through quantitative filter paper, and the solution was stored in PE bottles to complete the digestion.

### III. D. 2) Disintegration methods for water samples

Extract 5mL of water samples, add aqua regia 5mL and water samples in the colorimetric tube in the water bath heating (aqua regia configuration: pure water, concentrated hydrochloric acid, concentrated nitric acid in the proportion of 4:1:3 to be equipped), every half an hour on the reagents containing the test tube shaking operation, to ensure that the full response to the elimination process lasts for 1.3 hours, the reaction is completed after the cooling of the static, add 5ml of hydrochloric acid and then use ultrapure water to 25 ml, the volume of water to 25 ml. Filtered in PE plastic bottles and stored for testing.

### III. D. 3) Elimination methods for soil samples

Weigh 0.5 g of soil sample in a clean 50 ml ablation tube, 5 ml of concentrated nitric acid was added to the ablation tube, placed on the ablator and left overnight. Heating up procedure: firstly, adjust the temperature of the ablator to 60°C, keep it for 30min, continue to increase the temperature to 90°C and keep it for 30min, then increase the temperature to 120°C, keep it at this temperature for 2h until the solution becomes translucent light yellow. Remove the ablation tube and place it on the ablation tube rack for cooling. After cooling, the solution was fixed to 25 ml with ultrapure water and then filtered into 100 ml clean PE plastic bottles and stored for measurement. The heavy metal concentrations in all the digests were determined by inductively coupled plasma emission spectrometry (ICP-OES) or graphite furnace atomic absorption spectrometry.

### III. E. Data analysis

A similar response ratio (  $RR$  ) was used as an effect value to measure the removal of heavy metal wastewater by the artificial wetland system, which was calculated by the formula:

$$RR = \ln\left(\frac{C_e}{C_i}\right) = \ln C_e - \ln C_i \quad (1)$$

where  $C_i$  is the average heavy metal concentration at the inlet of the artificial wetland, and  $C_e$  is the average heavy metal concentration at the outlet of the artificial wetland. When  $RR > 0$  indicates a negative change, i.e., there are heavy metals entering the effluent. When  $RR < 0$  indicates a positive change, i.e., there are heavy metals removed from the sewage. And when  $RR = 0$  indicates no effect, i.e. the artificial wetland system has no effect on the removal of this heavy metal. Its variance is:

$$v = \frac{S_e^2}{N_e C_e^2} + \frac{S_i^2}{N_i C_i^2} \quad (2)$$

where  $N_e$  and  $N_i$  are the sample sizes of heavy metal concentrations in the effluent and influent of the artificial wetland, respectively, and  $S_e$  and  $S_i$  are the standard deviations of heavy metal concentrations in the effluent and influent of the artificial wetland, respectively.

The combined effect value (  $RR_{++}$  ) was calculated by weighted calculation using the random effect model with the following formula:

$$RR_{++} = \frac{\sum_{i=1}^k W_i^* RR_i}{\sum_{i=1}^k W_i^*} \quad (3)$$

where  $k$  is the number of studies,  $W_i^*$  is the inverse of the total study variance (  $V_{RR++}$  ), and  $V_{RR++}$  is the sum of the within- and between-study variances, which is given by:

$$V_{RR++} = (v + T^2) \quad (4)$$

$$T^2 = \frac{Q - df}{\sum W_i - \frac{\sum W_i^2}{\sum W_i}} \quad (5)$$

$$Q = \sum_{i=1}^k W_i RR_i^2 - \frac{\left( \sum_{i=1}^k W_i RR_i \right)^2}{\sum_{i=1}^k W_i} \quad (6)$$

where  $W_i$  is the inverse of the variance of a single study, i.e.,  $1/v$ .

In order to better illustrate the removal effect of the artificial wetland system on heavy metals in wastewater, the above combined effect value was converted to the combined removal rate, which was calculated as follows:

$$\text{Comprehensive removal rate} = [1 - \exp(RR_{++})] \times 100\% \quad (7)$$

The 95% confidence intervals (95% CI) for  $RR_{++}$  were generated by MetaWin software iteratively run 64599 times. If the 95% CI does not include 0, it indicates that the artificial wetland system has a significant effect on the combined removal of heavy metals from wastewater ( $P < 0.05$ ). If the 95% CI includes 0, it means that the effect of artificial wetland system on the combined removal rate of heavy metals in wastewater is not significant ( $P > 0.05$ ).

The stability of the effect of artificial wetland on the removal of heavy metals in sewage was measured by the size of the confidence interval of the combined removal rate, and the smaller the confidence interval, the more stable the removal effect.

## IV. Removal of complex heavy metals by artificial wetlands

### IV. A. Removal effects of different substrate configurations

Changes in effluent water quality and the effect of nitrogen and phosphorus removal are shown in Table 3.

The  $pH$  of each device gradually decreased. Among the four groups of artificial wetlands, the  $pH$  of the biochar group was higher than that of the zeolite group, while that of the zeolite-biochar group was higher than that of the former two, indicating that the combined addition of zeolite and biochar could significantly improve the effluent  $pH$ .

The DO mass concentration in the effluent water of wetlands CK, F, S and FS was significantly lower than that of the influent water ( $P < 0.05$ ), which showed a low-oxygen condition. Among the corresponding effluent  $COD$  values, the FS group had a  $COD$  value of  $7.85 \pm 6.03$ , which was lower than that of the other three groups, and the removal effect was better.

Table 3: Water quality change and removal of nitrogen and phosphorus

	$COD_I (mg \cdot L^{-1})$	$pH$	$DO_I (mg \cdot L^{-1})$	$NO_3^- - N_I (mg \cdot L^{-1})$	$NH_4^+ - N_I (mg \cdot L^{-1})$	$TN_I (mg \cdot L^{-1})$	$TP_I (mg \cdot L^{-1})$
CK	$15.23 \pm 3.45a$	$6.65 \pm 0.23c$	$0.58 \pm 0.34a$	$0.56 \pm 0.34c$	$5.96 \pm 3.25a$	$6.34 \pm 2.84a$	$2.01 \pm 1.35a$
F	$12.45 \pm 4.11b$	$6.61 \pm 0.23d$	$0.56 \pm 0.35a$	$0.89 \pm 1.31c$	$5.19 \pm 4.56b$	$5.99 \pm 4.31b$	$1.99 \pm 1.52a$
S	$11.03 \pm 5.03c$	$6.75 \pm 0.14b$	$0.48 \pm 0.39a$	$1.16 \pm 1.25a$	$5.67 \pm 4.87a$	$6.65 \pm 4.94a$	$1.95 \pm 1.14a$
FS	$7.85 \pm 6.03d$	$6.84 \pm 0.16a$	$0.52 \pm 0.53a$	$0.91 \pm 0.72b$	$3.96 \pm 3.34c$	$4.89 \pm 3.48b$	$1.81 \pm 0.98b$

The average removal rates of effluent water quality indicators are shown in Table 4. The values of CK, F, S and FS in the wetland effluent were 0.9052, 0.9286, 0.9469 and 0.9615, respectively, indicating that the addition of zeolite and biochar could significantly increase the removal rate of oxygen-depleting organic matter ( $P < 0.01$ ), and the joint addition had the best removal effect.

Table 4: Average removal rate of water quality

Handling	$COD$	$NO_3^- - N$	$NH_4^+ - N$	$TN$	$TP$
CK	0.9052	0.9725	0.7685	0.8964	0.6021
F	0.9286	0.9601	0.7898	0.9005	0.6235
S	0.9469	0.9417	0.7614	0.8893	0.6489
FS	0.9615	0.9713	0.8547	0.9216	0.6942



#### IV. B. Combined removal rates for different substrate configurations

The combined removal rates of  $Cr$ ,  $Cd$ ,  $Cu$ ,  $Pb$  and  $Zn$  by wetland types with different substrate configurations are shown in Table 5.

From the analysis results of the integrated removal rates of  $Cr$ ,  $Cd$ ,  $Cu$ ,  $Pb$  and  $Zn$  by the artificial wetland systems with different substrate configurations, it can be seen that, for the heavy metal  $Cd$ , the wetland FS has the highest integrated removal rate of 86.92%, and the removal effect is stable as shown by the difference of the confidence interval. Wetland CK, on the other hand, had the lowest integrated removal rate of 61.27% and the most unstable removal effect. Wetland F and wetland S had similar combined removal rates of 70.34% and 72.36%, respectively.

The combined removal rates of wetlands CK, F, S and FS showed that the combined removal rates of artificial wetland systems with different substrate configurations for the same heavy metal varied significantly, and the maximum difference in the combined removal rate of different types of artificial wetlands for  $Cr$  was about 10%.

Table 5: Analysis of total removal rate

Heavy metal	Handling	Total removal rate/%	Freedom/df	95% confidence interval /%	
$Cd$	CK	0.6127	5	42.65	86.14
	F	0.7034	2	-43.02	88.55
	S	0.7236	12	42.75	92.87
	FS	0.8692	10	82.99	97.06
$Cr$	CK	0.6705	8	36.89	86.75
	F	0.5933	9	-21.53	80.91
	S	0.6718	12	45.96	82.14
	FS	0.7261	12	76.85	91.25
$Cu$	CK	0.5426	1	36.56	72.51
	F	0.6123	6	45.96	85.69
	S	0.6536	12	47.02	86.02
	FS	0.6805	10	62.19	90.83
$Pb$	CK	0.5961	9	24.54	70.59
	F	0.5443	6	36.98	75.87
	S	0.8661	12	45.69	91.54
	FS	0.8257	21	80.17	93.87
$Zn$	CK	0.6563	4	20.54	78.23
	F	0.5469	9	36.95	82.52
	S	0.6895	2	43.16	87.01
	FS	0.7251	4	71.09	93.53

#### IV. C. Distribution of heavy metals in artificial wetlands

The contents of heavy metals in different parts of *Acorus calamus* are shown in Table 6. All five heavy metals accumulated less in *Acorus calamus* and were mainly enriched in the underground part ( $P < 0.05$ ).

The bioabsorption coefficient of the five heavy metals in wetland CK was the largest, which was about twice that of the remaining three groups of artificial wetlands. It indicated that the addition of zeolite and biochar could both reduce the uptake of heavy metals by *Acorus calamus* ( $P < 0.05$ ). The transfer coefficients of the five heavy metals were less than 1, which indicated that the heavy metals circulated less in *Acorus calamus* and were mainly accumulated in the underground part.

The biotransfer coefficients for  $Cr$ ,  $Pb$  and  $Cd$  were the smallest in all installations. It indicates that  $Cr$ ,  $Pb$  and  $Cd$  were mainly removed by inter-root interception to minimize the damage to the aboveground.  $Zn$  and  $Cu$  were removed to avoid over-concentration in the aboveground while meeting the requirements of growth and metabolism, which is consistent with the results that the plant height of *Acorus calamus* in all the installations increased along with the biomass of the aboveground and below-ground parts of the plant at the end of the experiment.

Table 6: The amount of heavy metals in different parts of the calamus

Handling	Site	$Cu$ / $mg \cdot kg^{-1}$	$Zn$ / $mg \cdot kg^{-1}$	$Pb$ / $mg \cdot kg^{-1}$	$Cd$ / $mg \cdot kg^{-1}$	$Cr$ / $mg \cdot kg^{-1}$
CK	On the ground	$356.75 \pm 14.235$	$436.26 \pm 14.11$	$113.24 \pm 14.81$	$52.45 \pm 6.58$	$108.24 \pm 8.89$
	Underground	$1289.26 \pm 221.34$	$1678.15 \pm 378.64$	$816.24 \pm 271.36$	$372.75 \pm 71.24$	$732.45 \pm 8.12$
F	On the ground	$251.26 \pm 38.21$	$356.78 \pm 91.25$	$64.58 \pm 23.07$	$38.46 \pm 8.12$	$92.18 \pm 12.66$
	Underground	$745.65 \pm 20.07$	$1145.63 \pm 42.23$	$461.21 \pm 52.96$	$350.49 \pm 1.11$	$542.31 \pm 25.77$
S	On the ground	$378.12 \pm 72.96$	$468.69 \pm 12.08$	$113.84 \pm 4.03$	$60.48 \pm 1.05$	$128.69 \pm 15.42$
	Underground	$946.52 \pm 275.56$	$1205.63 \pm 145.22$	$437.26 \pm 85.45$	$278.65 \pm 60.84$	$490.62 \pm 20.14$
FS	On the ground	$327.54 \pm 15.28$	$392.12 \pm 17.34$	$109.25 \pm 2.36$	$50.61 \pm 1.82$	$118.95 \pm 2.34$
	Underground	$1182.63 \pm 186.59$	$1453.26 \pm 256.19$	$543.72 \pm 88.01$	$389.64 \pm 74.52$	$589.39 \pm 14.02$

#### IV. D. Cd purification efficiency and retention flux in wetland systems

The wetland system Cd interception fluxes are shown in Table 7.

After purification by the simulated artificial wetland system, the Cd output fluxes of the wetland CK, F, S and FS treatments were  $0.72 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ ,  $0.64 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ ,  $0.23 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ ,  $0.28 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ .

The Cd interception fluxes of plants during purification were  $0.94 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ ,  $1.25 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ ,  $1.63 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ ,  $2.17 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ .

The sediment Cd interception fluxes were  $4.12 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ ,  $4.26 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ , and  $4.33 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ ,  $4.84 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ . In terms of the retention efficiency, the percentage of sediment retention was above 70%, indicating that sediment adsorption and bioflocculation and precipitation play a major role in this system to purify Cd from the simulated wastewater.

Table 7: Wetland system Cd stop flux

	Plant latency / $mg$	Plant flux / $mg \cdot (\text{m}^2 \cdot \text{d})^{-1}$	Sediment retention / $mg$	Sediment flux / $mg \cdot (\text{m}^2 \cdot \text{d})^{-1}$	Output / $mg$	Output flux / $mg \cdot (\text{m}^2 \cdot \text{d})^{-1}$
CK	71.52	0.94	256.84	4.12	50.23	0.72
F	87.26	1.25	223.05	4.26	49.31	0.64
S	102.25	1.63	235.67	4.33	42.34	0.23
FS	121.83	2.17	259.33	4.84	43.02	0.28

#### IV. E. Role of plants

The removal of heavy metal ions by plants is mainly reflected in the root secretion, root oxygen secretion and the absorption and transportation of plants themselves. The growth of plants in artificial wetland+microbial fuel cell is easily affected by the conditions of temperature, light and pH.

##### (1) Role of plant root secretion

Some metabolites secreted by plant roots can change the inter-root environment, thus activating, passivating or changing the valence state of heavy metal ions and reducing the toxicity of heavy metals in wastewater. At the same time, the plant root system will also influence the microorganisms to form mycorrhiza to enhance the absorption of heavy metals by plants.

##### (2) Oxygen secretion by plant root system

After photosynthesis, the oxygen produced by plants will be transported to the inter-root, which increases the dissolved oxygen content of the substrate near the root system, this phenomenon is called root oxygen secretion (ROL).

On the one hand, sufficient dissolved oxygen in the water column makes the oxidized state of heavy metals high, enhances their solubility and mobility, and promotes the uptake of heavy metals by wetland plants.

On the other hand, the ROL process increases the redox potential in the inter-root region, which promotes the power production of the artificial wetland technology + microbial fuel cell technology as well as the removal of pollutants by anode microorganisms.

##### (3) Plant enrichment



The removal of heavy metals from water bodies is achieved by the continuous accumulation of heavy metals in plants through uptake and translocation. Most of the heavy metal ions enter the plant root cells through metal transporter proteins and are further transported to the vesicle storage in the plant. Relevant studies found that water hyacinth possesses a stronger enrichment capacity than false iris when artificial wetland technology + microbial fuel cell technology configuration treats wastewater containing *Ni* and *Zn*, and the enrichment of the root system is much larger than that of the stems and leaves.

## V. Conclusion

This paper focuses on the removal effect of artificial wetland systems with different substrate configurations on composite heavy metals. By forming four groups of artificial wetlands and comparing the effluent water quality, the average removal rate of effluent water quality indicators was calculated. Obtain the combined removal rates of different substrate configurations of wetland types on *Cr*, *Cd*, *Cu*, *Pb* and *Zn*.

(1) The artificial wetland systems composed of different ratios of gravel, zeolite and biochar could all reduce the *pH* value in the effluent water quality. among the four groups of artificial wetlands, the *pH* of the biochar group was higher than that of the zeolite group, and the zeolite-biochar group was higher than that of the former two, which indicated that the combined addition of zeolite and biochar could significantly increase the effluent water *pH*.

(2) The wetland plants were selected from the wild calamus, and the adsorption results of heavy metals in the artificial wetland system showed that the accumulation of all five heavy metals in the calamus was low, and the heavy metals were mainly enriched in the underground part. The retention rate of wetland CK, F, S and FS on *Cd* sediment reached more than 70%, and the wetland plants accumulated heavy metals in the plants by absorbing and transferring heavy metals, thus realizing the removal of heavy metals from the water body.

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