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Removal Efficiency of Heavy Metals Such as Lead and Cadmium by Different Substrates in Constructed Wetlands

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Abstract: In order to find an efficient and economical wetland substrate to treat mine wastewater containing various heavy metals, and effectively realize the resource utilization of water treatment residuals, in this paper, the treatment efficiency of mine wastewater containing various heavy metals was investigated using unburned ceramsite prepared from water treatment residuals (UCWTR) and clay ceramsite. The continuous dynamic test results showed that the removal rate of Pb, Cd, Cu, Zn, and Fe can reach more than 98.5% after the UCWTR-based CWs runs for 56 days, and its concentration was 30.05%, 24.85%, 20.82%, 14.63%, and 7.91% lower than that of the clay ceramsite-based CWs, respectively. SEM, XPS, and FT-IR showed that the characteristic peaks of two ceramsites were basically similar. The ceramsite undergoes ion exchange, coordination complexation, and chelation reaction with Pb, Cd, Cu, Zn, and Fe under the action of the gel of internal groups -OH, C=O, Al-OH, Si-Fe-O and C-S-H. Compared with clay ceramsite, the ion exchange reaction and chelation reaction of -OH effect and the coordination reaction of C=O effect of carboxyl group in UCWTR were enhanced. In conclusion, using UCWTR as a CWs substrate can effectively enhance the adsorption capacity of heavy metals, providing a scientific basis for the application of UCWTR-based CWs in mine wastewater treatment.

Keywords: water treatment residuals; unburned ceramsite; mine wastewater; constructed wetlands; lead; cadmium

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1. Introduction

According to statistics, the annual discharge of mine wastewater reaches 1.2–1.5 billion tons in China, accounting for about 30% of the total wastewater from the non-ferrous metal industry. Among them, the discharge of acid mine drainage (AMD) generated after coal mining has become a prominent environmental pollution problem in the environmental management of mining areas [1]. The composition of mine wastewater is complex, containing a variety of heavy metal ions and suspended solids. In addition, heavy metals have concealment, bioaccumulation, carcinogenicity, and chemical toxicity, and trace amounts can damage biological safety [2]. As a class I pollutants, low concentrations of Pb and Cd can cause the leaves of plants to wither and reduce the number of lateral roots, while high concentrations can inhibit plant photosynthesis, damage cells, and even cause plant death [3,4]. According to the removal mechanism of heavy metals in mine wastewater, treatment technologies can be divided into two types: physicochemical treatment technology and biological treatment technology. Using a single physicochemical method to treat mine wastewater will lead to problems such as high cost, high energy consumption, and possible secondary pollution. Similarly, single biological treatment will also have problems such as unstable treatment effect, long period and large environmental impact. Therefore, compared with the traditional treatment technology, the constructed wetlands (CWs) have the characteristics of long-term operation, simple management, and long service time, and has a good application prospect in mine wastewater treatment.

Existing studies have found that CWs are mainly used in the treatment of organic wastewater such as landfill leachate [5], rural sewage [6], and aquaculture wastewater [7]. The main treatment indexes include chemical oxygen demand (COD), ammonia nitrogen (NH4-N) [8], total nitrogen (TN) [9], total phosphorus (TP) [10], and other pollutants, while there are relatively few studies on heavy metal wastewater [11]. It is speculated that the main reason is the poor removal of heavy metals by CWs, the less adsorption of substrates, the slow enrichment effect of plants, and the long treatment period, resulting in the limited application of CWs in the purification of heavy metal wastewater [12]. Therefore, it is imperative to select high-quality CWs substrate to improve the adsorption capacity of the CWs and enhance the treatment efficiency and purification effect of heavy metals. Liu et al. [13] used the vertical subsurface flow CWs to purify the wastewater containing Cd, and found that the removal rate of NO_3-N and Cd^{2+} in the wetland reached more than 80%. Liang et al. [14] used the porous slag CWs to treat the saline wastewater containing various heavy metals. The results showed that the CWs were effective for treatment of Cu, Zn, Cd, and Pb in the wastewater, and could enhance the enrichment effect of plants on heavy metals. Arivoli et al. [15] used vertical subsurface flow CWs to treat multiple heavy metal ions in paper-making wastewater. The results showed that the removal rates of Fe, Cu, Mn, Zn, Ni, and Cd in CWs were 74%, 80%, 60%, 70%, 71%, and 70%, respectively. Saeed et al. [16] used a combination of vertical subsurface flow CWs and horizontal subsurface flow CWs to treat Zn, Cr, Ni, and Pb in landfill leachate. It was found that the removal rates of Zn, Cr, Ni, and Pb in wastewater by the combined CWs were 20–97%, 95–99%, 55–73%, and 69–83%, respectively.

Water treatment residuals (WTR) are a safe waste produced during the treatment of drinking water sources and have been proven to be an environmentally friendly material [17]. Direct landfill treatment will not only cause loss of land resources, endanger the surrounding environment of the landfill, but also lead to waste of resources [18]. In the early stage, our research team has successfully prepared unburned ceramsite from water treatment residuals. Compared with the clay ceramsite sintered at high temperature, UCWTR has higher content of active iron and aluminum, larger porosity and specific surface area, and higher mechanical strength [19]. It is also used as an adsorption material to explore the adsorption performance [20] and regeneration [21] of lead and cadmium. The results showed that the maximum adsorption capacity of UCWTR for lead and cadmium can reach 13.48 mg/g and 17.88 mg/g, respectively [20]. It had great potential to be used as the substrate of CWs for the treatment of heavy metal polluted water [22]. Therefore, our study used UCWTR as the CWs substrate to explore the treatment efficiency of UCWTR-based CWs for heavy metal pollutants in mine water, in order to further reveal the key influencing factors and mechanisms of UCWTR to enhance the removal of heavy metals in CWs, in order to provide a scientific basis and technical support for UCWTR-based CWs to treat mine wastewater.

2. Materials and Methods

2.1. Substrates' Samples

The raw material WTR is collected from a water plant in Hunan. According to the configuration method of the previous team [19], WTR is mixed with fly ash, cement, quicklime, and gypsum at 60%, 20%, 15%, 2.5%, and 2.5% to make UCWTR, and then air-dried for 10 h in a constant temperature water bath at 85 °C. The comparative ceramsite is high temperature calcined clay ceramsite.

The main components of UCWTR and ceramsite obtained by XRF are shown in Table 1.

Table 1. Main components of ceramsites.

Sample	pH	Si/%	Al/%	Fe/%	Ca/%	Mg/%	Na/%	K/%	S/%
UCWTR	9.61	41.19	14.56	10.25	26.07	1.13	1.41	3.41	1.86
Clay ceramsite	7.03	50.21	11.53	5.15	21.37	6.78	2.57	2.14	0.25

The main characteristic parameters of UCWTR and clay ceramsite obtained are shown in Table 2.

Table 2. Characteristic parameters of UCWTR and clay ceramsite.

Features	UCWTR	Clay Ceramsite
Particle size	5–8 mm	5–8 mm
Porosity	$\geq$42%	$\geq$33%
Wear rate	3.2%	2.2%
Water absorption	$\geq$30%	$\geq$30%
Hydrochloric acid solubility	2%	2%
Mud content	0.5%	0.3%
Bulk density	900–950 kg/m^3	900–980 kg/m^3
Apparent density	1000–1200 kg/m^3	1000–1200 kg/m^3
Cylinder strength	>4.0 Mpa	>4.0 Mpa

2.2. *Wastewater Preparation and Analysis*

The experimental influent was prepared according to the detection results of wastewater components from a lead-zinc mine in Yueyang City, Hunan Province, where the concentrations of Pb, Cd, Cu, Zn, Fe, and sulfate (calculated as SO_4^{2-}) were 12.9 mg/L, 7.5 mg/L, 23.0 mg/L, 47 mg/L, 18.3 mg/L, and 66.1 mg/L, respectively. The CWs were fed with synthetic wastewater through the entire experimental period. After treatment, the contents of heavy metal, dissolved oxygen (DO), and pH from influent and effluent samples were measured by an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) method, a portable dissolved oxygen meter method, and a pH meter method.

2.3. *Wetland System and Operation*

In this study, a CWs dynamic experimental device was constructed to compare the Pb and Cd removal efficiency of various substrates. Figure 1 illustrates the CWs system consisting of a storage tank with synthetic wastewater, a peristaltic pump, two CWs units, a blower, an electric box, and two effluent tanks. Two groups of horizontal subsurface flow CWs reactors were made of plexiglass with a length of 1 m, a width of 0.5 m, and a height of 0.8 m, which was filled with 0.1 m gravel as the supporting layer, and the upper part of the gravel was filled with the selected substrates. The horizontal direction of the reactor set an outlet every 0.2 m, and one group of electronic probes was placed every 0.2 m along the top of the water flow as an online analysis. Real-time monitoring took place of pH value and DO of wastewater each hour, and the water environment chemical changes in the reactor were monitored in real time. *Canna indica* L. seedlings had similar growth on the top of the reactor.

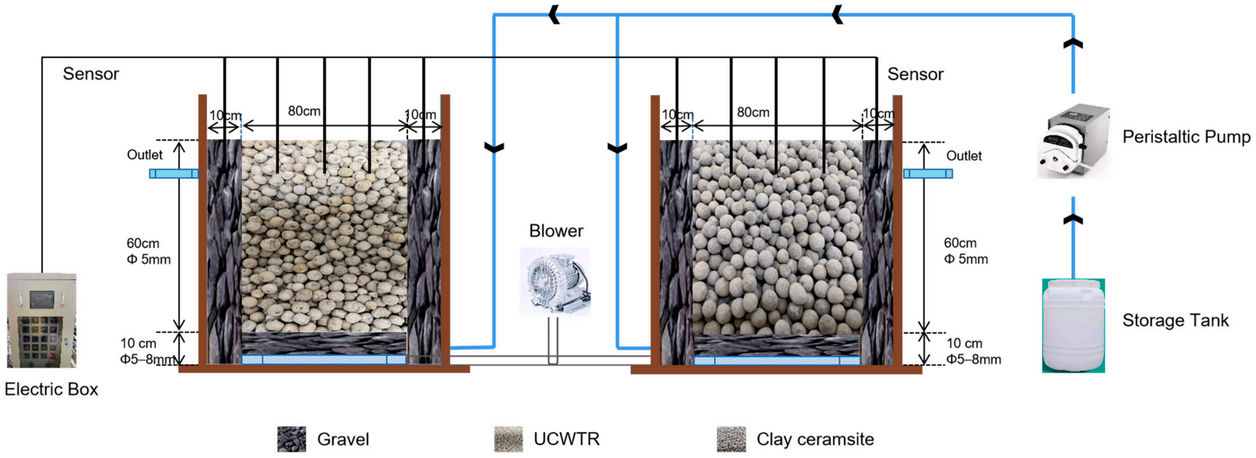


Figure 1. Schematic diagram of a simulated CWs device.

In addition, 200 kg of UCWTR and clay ceramsite were filled in the two groups of CWs reactors to maintain a slope of about 1% on the surface. *Canna indica* L. with the same growth trend was selected to be planted on the surface of CWs with the planting density of 16 plants/m^2 after being cultured in clear water for 3 days. The high-pressure sodium lamp was used to simulate the sunlight in the middle of the two groups, and the light time was set to 9 h to meet the needs of plant light.

Before the test, we first injected the improved Hongland nutrient solution into the storage tank for adaptive cultivation of *Canna indica* L. After 30 days of running, the prepared mine wastewater instead of the Hongland nutrient solution was injected into the storage tank of CWs. In this experiment, the mode of operation in the CWs experiments was horizontal subsurface flow, the pH value of influent was controlled to be about 6–8, the instantaneous aeration rate was 0.5 L/min, the intermittent aeration was 6 h every day, the influent flow was 0.04 L/min, and the hydraulic retention time (HRT) was set at 2 d. The concentrations of Pb, Cd, Cu, Zn, and Fe at the water inlet, water outlet, and along the way were measured every 2 days to investigate the treatment efficiency of UCWTR-based CWs for mine wastewater containing various heavy metals. In addition, the concentration changes of Pb, Cd, Cu, Zn and Fe in the effluent of the two groups of units under different HRT were investigated.

3. Results

3.1. Characteristics of UCWTR-Based CWs for Heavy Metal Wastewater

3.1.1. Heavy Metal Content in the Horizontal Direction

(1) Pb

The changes of Pb concentration along the horizontal direction with the running time of the two groups of devices are shown in Table 3. During this period of operation, with the increase of horizontal distance, the concentration of Pb gradually decreased along the route, and the removal rate of Pb in wastewater by both sets of devices was above 98%. Compared with the clay ceramsite-based CWs, the Pb concentration of each outlet of the UCWTR-based CWs was lower. On the 2nd, 10th, 20th, 30th, 40th, and 50th days, the substrate distance increased from 0.2 m to 0.8 m, and the Pb concentration in the effluent of UCWTR-based CWs decreased by 88.89%, 34.01%, 89.75%, 87.16%, 29.89%, 92.44%, and the Pb concentration in the effluent of the clay ceramsite-based CWs decreased by 100%, 55.37%, 93.49%, 88.80%, 34.29%, and 74.82%, respectively. With the prolongation of operation time, the concentration of Pb in the water intake of UCWTR-based and clay ceramsite-based CWs increased. After 50 days of operation, the concentration of Pb at 0.2 m, 0.4 m, and 0.6 m increased to 18.41, 4.91, 2.19 times and 4.06, 2.83, 1.43 times that of the 40th day, and the removal rate of Pb in wastewater was still above 98.7%. After running for 50 d, the first 0.2 m of ceramsite in the two devices can still remove more than 98% of Pb in the wastewater [23], indicating that the two ceramsites have strong adsorption capacity for Pb [24].

Table 3. Change in horizontal Pb concentration at 2 d, 10 d, 20 d, 30 d, 40 d, 50 d (mg/L).

Substrates	Time/d	Horizontal Distance/m				
		0	0.2	0.4	0.6	0.8
UCWTR	2	12.75	0.005	0.003	0.002	0
	10	12.60	0.007	0.009	0.002	0.004
	20	13.01	0.050	0.023	0.019	0.006
	30	13.01	0.050	0.023	0.019	0.006
	40	12.50	0.009	0.008	0.008	0.006
	50	13.00	0.169	0.038	0.018	0.013
Clay ceramsite	2	13.10	0.006	0.002	0.001	0
	10	12.55	0.011	0.007	0.015	0.005
	20	12.79	0.111	0.013	0.014	0.006
	30	13.05	0.095	0.043	0.014	0.010
	40	12.78	0.017	0.013	0.012	0.011
	50	13.09	0.063	0.036	0.018	0.016

(2) Cd

The changes of Cd concentration along the horizontal direction with the running time of the two groups of devices are shown in Table 4. During this period, the Cd concentration gradually decreased with the increase of the horizontal distance, but with the extension of the operation time, the Cd concentration of each outlet showed an increasing trend, and the Cd removal rate continued to maintain above 90%. In the early stage of operation (2–40 d), the Cd concentration in the water intake along the way changed little, but the removal rate was all above 98%. This indicates that, in the first 40 d, the ceramsite at the first 0.2 m adsorbed more than 98% of the Cd in the solution, and the ceramsite at the rear section of the device plays a small role. On the 2nd, 10th, 20th, 30th, 40th, and 50th days, the substrate distance increased from 0.2 m to 0.8 m, and the Cd concentration in the effluent of UCWTR-based CWs decreased by 99.68%, 81.69%, 69.02%, 86.68%, 72.09%, 98.44%, and the Cd concentration in the effluent of the clay ceramsite-based CWs decreased by 95.83%, 72.37%, 74.70%, 79.94%, 77.58%, and 98.07%, respectively. On the 50th day of operation, the Cd concentration at the water intakes of UCWTR based and clay ceramsite based CWs increased, and the Cd concentration at 0.2, 0.4, and 0.6 m increased to 14.94, 3.64, 3.57 times and 12.96, 6.89, 4.88 times of the 40th day, respectively. This result may be due to the strong electronegativity, small hydration radius, and weak competitive adsorption capacity of Cd. The active sites on the ceramsite in the front section were occupied by other heavy metal ions, resulting in weak competitive adsorption of Cd on the ceramsite and increased Cd concentration in the effluent.

Table 4. Change in horizontal Cd concentration at 2 d, 10 d, 20 d, 30 d, 40 d, 50 d (mg/L).

Substrates	**Time/d**	**Horizontal Distance/m**				
		0	**0.2**	**0.4**	**0.6**	**0.8**
UCWTR	2	7.45	0.155	0.074	0.022	0
	10	7.63	0.033	0.024	0.021	0.006
	20	7.63	0.055	0.017	0.013	0.007
	30	7.63	0.055	0.017	0.013	0.007
	40	7.56	0.052	0.034	0.024	0.014
	50	7.49	0.7708	0.124	0.084	0.012
Clay ceramsite	2	7.50	0.035	0.039	0.030	0
	10	7.68	0.029	0.024	0.021	0.008
	20	7.79	0.038	0.020	0.015	0.010
	30	7.64	0.063	0.037	0.017	0.013
	40	7.54	0.062	0.043	0.025	0.014
	50	7.03	0.793	0.308	0.129	0.016

(3) Cu

The changes of Cu concentration along the horizontal direction with the running time of the two groups of devices are shown in Table 5. With the increase of horizontal distance, the Cu concentration at each water intake gradually decreases, but with the extension of operation time, the Cu concentration at the corresponding water intake shows a fluctuating trend, and there was no obvious difference in the removal effect of Cu in wastewater between the two groups of devices. In the early stage of operation (the 2nd day), the Cu concentration at each water intake of UCWTR and clay ceramsite-based CWs was low, which was 0.98 mg/L, 0.25 mg/L, 0.13 mg/L, 0.05 mg/L and 0.39 mg/L, 0.19 mg/L, 0.08 mg/L, 0.04 mg/L, respectively.

Table 5. Change in horizontal Cu concentration at 2 d, 10 d, 20 d, 30 d, 40 d, 50 d (mg/L).

Substrates	**Time/d**	**Horizontal Distance/m**				
		0	**0.2**	**0.4**	**0.6**	**0.8**
UCWTR	2	22.89	0.985	0.245	0.131	0.052
	10	22.73	1.292	0.838	0.524	0.414
	20	22.70	1.495	1.033	0.822	0.616
	30	22.70	1.495	1.033	1.033	0.822
	40	22.69	0.697	0.501	0.314	0.261
	50	22.52	1.896	0.622	0.515	0.255
Clay ceramsite	2	22.85	0.390	0.193	0.082	0.038
	10	22.36	0.987	0.954	0.790	0.581
	20	22.77	1.523	0.866	0.326	0.219
	30	22.61	1.106	0.727	0.626	0.549
	40	23.12	0.615	0.521	0.432	0.254
	50	22.60	0.766	0.379	0.263	0.317

(4) Zn

The changes of Zn concentration along the horizontal direction with the running time of the two groups of devices are shown in Table 6. With the increase of the substrate distance, the Zn concentration gradually decreased along the route, but the Zn concentration of the corresponding water intake showed a fluctuating upward trend with time. On the 2nd, 10th, 20th, 30th, 40th, and 50th days, the substrate distance increased from 0.2 m to 0.8 m, and the Zn concentrations in the effluent of UCWTR and clay ceramsite-based CWs decreased by 94.87%, 77.56%, 85.04%, 93.70%, 77.18%, 91.46% and 96.67%, 57.96%, 90.43%, 79.63%, 55.44%, 99.75%, respectively. In the later period (50 d), the adsorption capacity of ceramsites to Zn in the first stage (0.2 m) decreased, the Zn concentration in the effluent of UCWTR and clay ceramsite-based CWs increased to 5.93 mg/L and 6.29 mg/L, and the removal rate dropped to 87.38% and 86.61%, respectively. However, the final (0.8 m) effluent Zn concentration (0.51 mg/L and 0.02 mg/L, respectively) still met the "Integrated Wastewater Discharge Standard (GB 8978-1996)".

Table 6. Change in horizontal Zn concentration at 2 d, 10 d, 20 d, 30 d, 40 d, 50 d (mg/L).

Substrates	**Time/d**	**Horizontal Distance/m**				
		0	**0.2**	**0.4**	**0.6**	**0.8**
UCWTR	2	47.01	1.042	0.478	0.337	0.054
	10	46.94	2.565	1.246	0.759	0.576
	20	47.90	4.359	0.820	0.478	0.275
	30	47.90	4.359	0.820	0.478	0.275
	40	47.27	1.028	0.473	0.403	0.235
	50	47.00	5.930	0.616	0.495	0.506
Clay ceramsite	2	46.89	1.290	0.518	0.216	0.052
	10	47.03	1.100	0.868	0.642	0.458
	20	47.75	2.010	0.820	0.308	0.191
	30	47.83	2.917	1.107	0.612	0.595
	40	46.99	1.251	0.709	0.655	0.571
	50	46.91	6.268	1.612	0.522	0.016

(5) Fe

The changes of Fe concentration along the horizontal direction with the running time of the two groups of devices are shown in Table 7. During the process of wastewater flowing through the substrate, the Fe concentration of each outlet gradually decreased. On the 2nd, 10th, 20th, 30th, 40th, and 50th days of operation, with the increase of the substrate distance, the Fe concentrations in the effluent of UCWTR and clay ceramsite-based CWs decreased by 81.86%, 83.27%, 87.52%, 60.28%, 77.478%, 79.32%, and 55.32%, 84.39%, 89.24%, 86.01%, 91.46%, 64.58%, respectively. During the entire operation period, the removal rate of Fe in the simulated wastewater by the two groups of devices remained at 88.50–99.77%, and the final effluent Fe concentration reached the “Integrated Wastewater Discharge Standard (GB 8978-1996)”. After running for 50 days, the first 0.2 m section of ceramsites can still remove more than 98% of Fe in wastewater, indicating that this section of ceramsites have a strong adsorption capacity for Fe and can effectively remove Fe in wastewater.

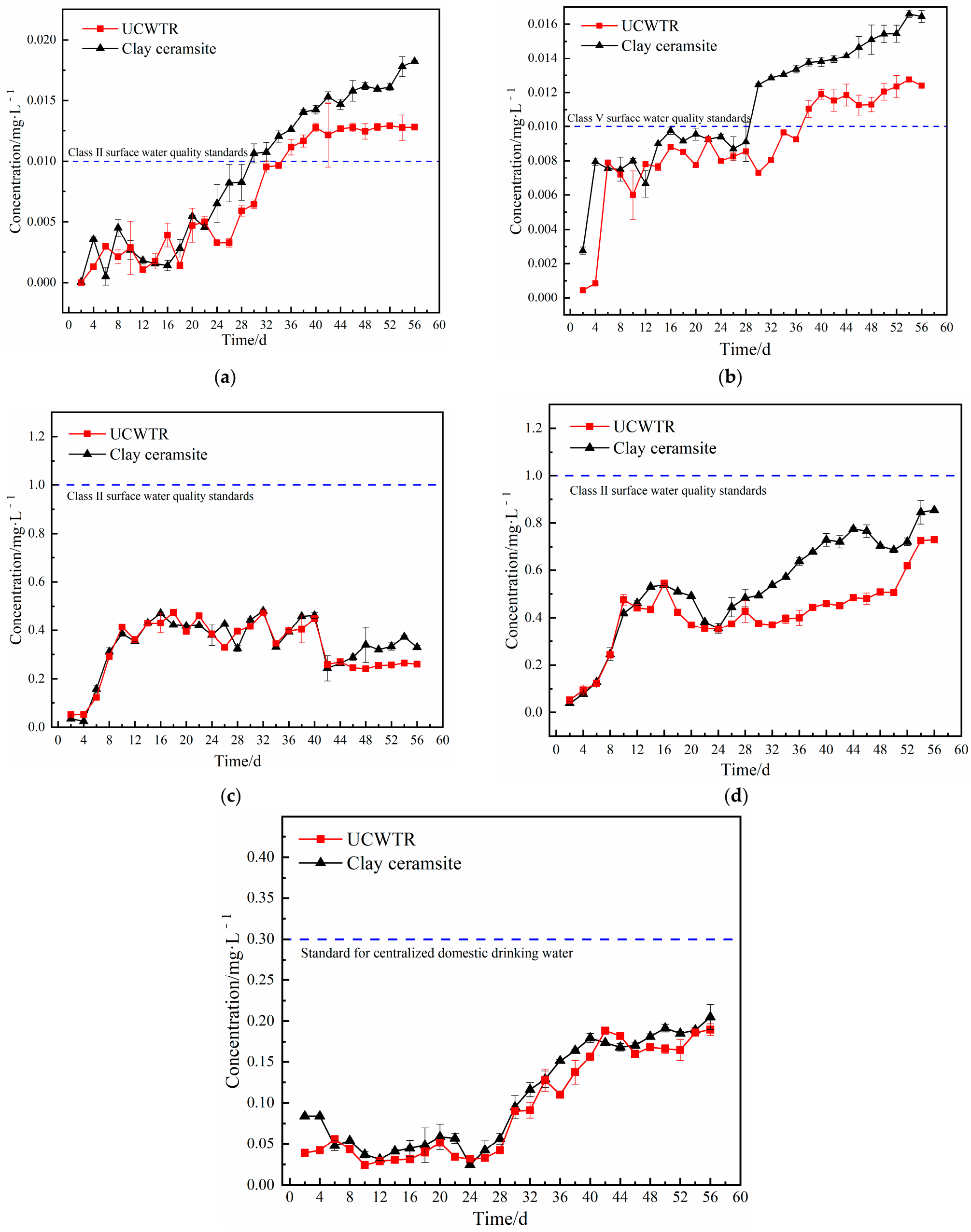
Table 7. Change in horizontal Fe concentration at 2 d, 10 d, 20 d, 30 d, 40 d, 50 d (mg/L).

Substrates	**Time/d**	**Horizontal Distance/m**				
		0	**0.2**	**0.4**	**0.6**	**0.8**
UCWTR	2	18.65	0.238	0.106	0.068	0.044
	10	18.20	0.146	0.067	0.032	0.025
	20	18.66	0.478	0.312	0.224	0.190
	30	18.66	0.616	0.381	0.262	0.210
	40	18.30	0.696	0.300	0.187	0.157
	50	18.24	0.804	0.238	0.191	0.166
Clay ceramsite	2	18.60	0.186	0.138	0.108	0.085
	10	18.21	0.252	0.066	0.055	0.045
	20	18.48	0.519	0.154	0.080	0.048
	30	18.71	0.749	0.365	0.121	0.085
	40	19.10	2.130	0.650	0.278	0.183
	50	18.06	0.725	0.178	0.120	0.188

3.1.2. Heavy Metal Content in Effluent Sample

When the average influent Pb concentration was 12.9 mg/L, the dynamic changes of the effluent Pb concentration after the two groups of horizontal subsurface flow CWs were operated continuously for 56 days are shown in Figure 2a. With the extension of the operation time, the average Pb removal rate of the two groups of units reached 99%, but the Pb concentration in the effluent first fluctuated and then gradually increased, and the Pb concentration in the effluent of the UCWTR-based CWs remained stable in the later period. During the whole operation period, the Pb concentration in the effluent of the two groups of units reached the “Integrated Wastewater Discharge Standard (GB 8978-1996)”. In the first 20 days, the Pb concentration in the effluent of the two groups of units fluctuated, and the average Pb concentrations in the effluent of UCWTR and clay ceramsite-based CWs were 0.0022 mg/L and 0.0024 mg/L, respectively. In the later stage, the Pb concentration in the effluent of CWs gradually increased, and the Pb concentration in the effluent of UCWTR and clay ceramsites-based CWs reached 0.0128 mg/L and 0.0183 mg/L on the 56th day. During the whole operation period, the removal rate of Pb in wastewater by the two groups of units reached more than 99.8%, and the removal rate of Pb in wastewater by UCWTR-based CWs continued to exceed 99.9%. The above results show that the two sets of devices have strong removal efficiency for Pb, and can continuously and efficiently purify Pb to make it meet the “Integrated Wastewater Discharge Standard (GB 8978-1996)”. In addition, UCWTR can enhance the removal efficiency of Pb in wastewater by CWs, and the overall effluent was lower than that of clay ceramsite-based CWs, and can maintain a stable removal effect in the later stage.

When the average influent Cd concentration was 7.5 mg/L, the dynamic change of effluent Cd concentration after 56 days of operation is shown in Figure 2b. With the extension of operation time, the two groups of CWs devices can basically absorb the Cd in the wastewater, and the effluent reaches the “Integrated Wastewater Discharge Standard (GB 8978-1996)”, but the effluent Cd concentration showed a fluctuating upward trend. Among them, the effluent Cd concentration of UCWTR and clay ceramsite-based CWs exceeds the class V standard of surface water on the 38th day and the 30th day, respectively. In the initial 6 days, the effluent Cd concentration of UCWTR-based CWs increased rapidly from 0.0005 mg/L to 0.0079 mg/L. On the 4th day, the effluent Cd concentration of clay ceramsite-based CWs increased from 0.0028 mg/L to 0.0080 mg/L. However, the removal rate of Cd by the two groups of devices was still above 99.89%. From the 6th day to the 28th day, the Cd concentrations in the effluent of UCWTR and clay ceramsite-based CWs showed a fluctuating trend, and the average concentrations were 0.0080 mg/L and 0.0086 mg/L, respectively. After that, the Cd concentration in the effluent of the two groups of units increased continuously and exceeded the class V standard of surface water. By the 56th day, the Cd concentration in the effluent of UCWTR and clay ceramsite-based CWs reached 0.0124 mg/L and 0.0165 mg/L, respectively, but the removal rate of Cd in the wastewater was still higher than 99.84% and 99.78%. Both kinds of ceramsite can absorb a large amount of Cd in wastewater, especially UCWTR. With the extension of operation time, other heavy metal ions compete with Cd for the surface active sites of ceramsite, resulting in a slight decrease in the adsorption capacity of ceramsite for Cd. However, the removal efficiency of the two groups of devices for Cd was still maintained at more than 99%.



(**a**) (**b**)

(**c**) (**d**)

(**e**)

Figure 2. Changes in effluent (**a**) Pb, (**b**) Cd, (**c**) Cu, (**d**) Zn, (**e**) Fe concentration.

When the average influent Cu concentration was 23.0 mg/L, the dynamic changes of the effluent Cu concentration of the two groups of horizontal subsurface flow CWs devices after continuous operation for 56 days are shown in Figure 2c. With the extension of operation time, the two groups of units can remove more than 97% of Cu in the wastewater, so that the effluent Cu concentration can meet the "Integrated Wastewater Discharge Standard (GB 8978-1996)". However, the overall Cu concentration showed a trend of rapid rise first and then fluctuation, and the effluent Cu concentration of UCWTR-based CWs remains stable in the later period. In the early stage of operation (0–10 days), the concentration of Cu in the effluent of UCWTR and clay ceramsite-based CWs increased rapidly to 0.4136 mg/L and 0.3855 mg/L, but the removal rate of Cu remained at 98.20% and 98.32%. On the 56th day, the Cu concentration in the effluent of UCWTR and clay ceramsite-based CWs remained at about 0.2609 mg/L and 0.3295 mg/L. During the whole operation period, both sets of devices can stably purify Cu in wastewater, indicating that the two kinds of ceramsite have large adsorption capacity and a stable effect on Cu.

When the average influent Zn concentration was 47 mg/L, the dynamic change of effluent Zn concentration is shown in Figure 2d. With the prolongation of operation time, both sets of devices can remove more than 97% of Zn in the wastewater, and the Zn concentration in the effluent reaches the "Integrated Wastewater Discharge Standard (GB 8978-1996)", but the Zn concentration shows a fluctuating upward trend as a whole. In the early stage of operation (0~10 d), the concentration of Zn in the effluent of UCWTR and clay ceramsite-based CWs increased rapidly by 8.89 times and 10.71 times. However, the growth rate slowed down in the later period. By the 56th day, the Zn concentration in the effluent of UCWTR and clay ceramsite-based CWs increased to 0.7294 mg/L and 0.8544 mg/L, respectively. The overall change trend of Zn concentration in the effluent was similar to that of Cd, which indicates that the adsorption behaviors of the two ceramsites to Cd and Zn were similar, and they are first adsorbed on the surface of ceramsite through electrostatic action. Then, under the action of -OH, Si-O-Si, Al-OH, etc., it further diffuses into the ceramsite, which may be related to the electronegativity of Cd and Zn, and the competitive adsorption capacity is quite related [25].

When the average influent Fe concentration was 18.3 mg/L, the dynamic changes of effluent Fe concentration after 56 days of operation are shown in Figure 2e. With the extension of the operation time, the two groups of units can remove more than 98% of Fe in the wastewater, and the Fe concentration of the effluent reaches the "Integrated Wastewater Discharge Standard (GB 8978-1996)", but the overall change of Fe can be divided into three stages of "fluctuation-rise-stability". In the early stage (0–24 d), the Fe concentrations in the effluent of the two groups of units fluctuated, with the average concentrations reaching 0.0373 mg/L and 0.0504 mg/L, respectively. In the later stage, the Fe concentration in the effluent of the two groups of units showed a rapid upward trend, and the Fe concentration in the effluent of UCWTR and clay ceramsite-based CWs increased to 0.1884 mg/L and 0.1736 mg/L by 42 d. After that, the concentration of Fe in the effluent of the two groups of units tended to be stable and maintained at about 0.18 mg/L. The overall change trend of Fe concentration in the effluent was similar to that of Pb, which indicates that the adsorption mechanism of Pb and Fe by the two ceramsites was similar. The reaction mechanism was to quickly adsorb on the surface of ceramsites, and then combine with the internal C-S-H gel to stabilize in the interior of ceramsites, which can efficiently and largely remove Fe and other pollutants in simulated wastewater.

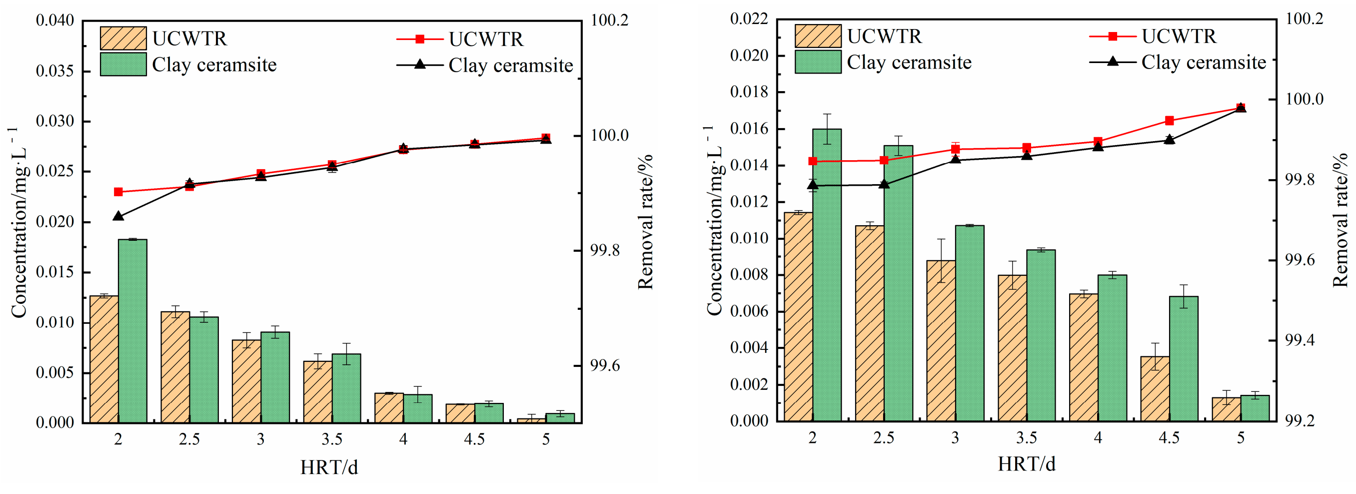
To sum up the experimental results, compared with other research results, for example, the removal rates of Cd, Zn, and Pb in mine wastewater by the combined technology of adsorption and CWs are 79.6%, 52.9%, and 38.7% [26]. Singh et al. [27] used organic matter improved CWs to treat mine wastewater in northern India, with a removal efficiency of 91.6% for heavy metal Fe. The CWs substrate used in this paper has better treatment efficiency of heavy metals, and the removal rate of heavy metals is above 99%. Compared with the clay ceramsite-based CWs, UCWTR based CWs have a better removal effect on heavy metals in the simulated mine wastewater and lower effluent concentration.

In particular, the effluent concentration of Pb and Cd is delayed for 6 days and 8 days, respectively, exceeding the class II and class V standards of surface water. This may be related to the high pH value and DO content in the UCWTR based CWs. The previous research findings also confirmed this result, that is, the increase of pH value is conducive to the adsorption of heavy metals Pb and Cd by ceramsites, and the increase of DO is beneficial to enhance the metabolic activity of plants. UCWTR was alkaline and has a large filling volume, which can effectively improve the pH value in the unit, maintain the long-term alkaline environment, and strengthen the purification effect of heavy metals in the CWs.

3.1.3. Optimization of Operating Parameters of UCWTR-Based CWs

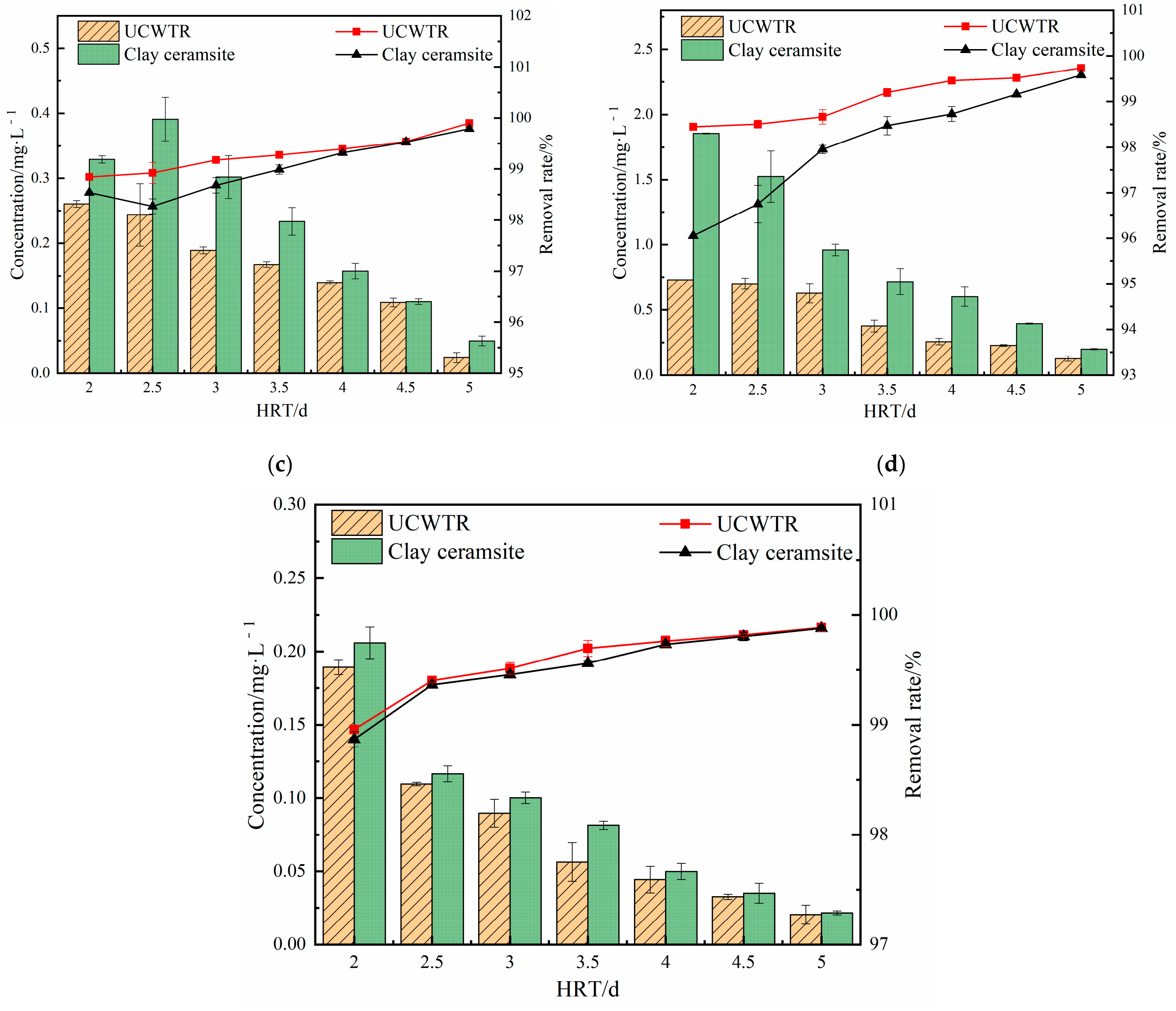
After 56 days of continuous operation, the concentrations of Pb, Cd, Cu, Zn, and Fe in the effluent of the two groups of units all showed an increasing trend, especially Cd, and the effluent concentration in the later stage could not meet the class V standard of surface water. Therefore, we investigated the change of heavy metal concentration in the effluent of the two groups of devices by adjusting the hydraulic retention time of the device, in order to provide a reference for the extended use of UCWTR-based CWs to treat heavy metals.

With the increase of HRT (2~5 d), the concentration of heavy metals in the effluent of the two groups of devices changes as shown in Figure 3. The concentrations of Pb, Cd, Cu, Zn, and Fe in the effluent of the two groups of devices were all inversely correlated with HRT. With the increase of HRT, the effluent concentration continued to decrease, but the removal rates of heavy metals were all above 95%. When HRT increased from 2 days to 5 days, the concentrations of Pb and Cd in the effluent of UCWTR and clay ceramsite-based CWs decreased from 0.013 mg/L, 0.011 mg/L and 0.018 mg/L, 0.016 mg/L to 0.003 mg/L, 0.0013 mg/L and 0.0009 mg/L, 0.0014 mg/L, decreased by 97.64%, 88.60% and 95.08%, 91.25%, respectively. The removal rates of Pb and Cd in the simulated wastewater of the two groups of devices were stable at above 99.7%, and the concentration of Pb and Cd in the effluent can meet the discharge standard when the HRT was 3 days, and the concentration of Cd in the effluent can also meet the discharge standard when the hydraulic retention time was 3.5 days. When HRT was extended to 5 days, the effluent Zn concentration of UCWTR and clay ceramsite-based CWs increased from 0.73 mg/L and 1.86 mg/L decreased to 0.13 mg/L and 0.20 mg/L, and the removal rate increased from 98.45% and 96.05% to 99.73% and 99.58%, respectively. Regardless of the HRT changes, the concentration of Cu and Fe in the effluent can meet the "Integrated Wastewater Discharge Standard (GB 8978-1996)".



(**a**) (**b**)

Figure 3. *Cont.*



(c)

(d)

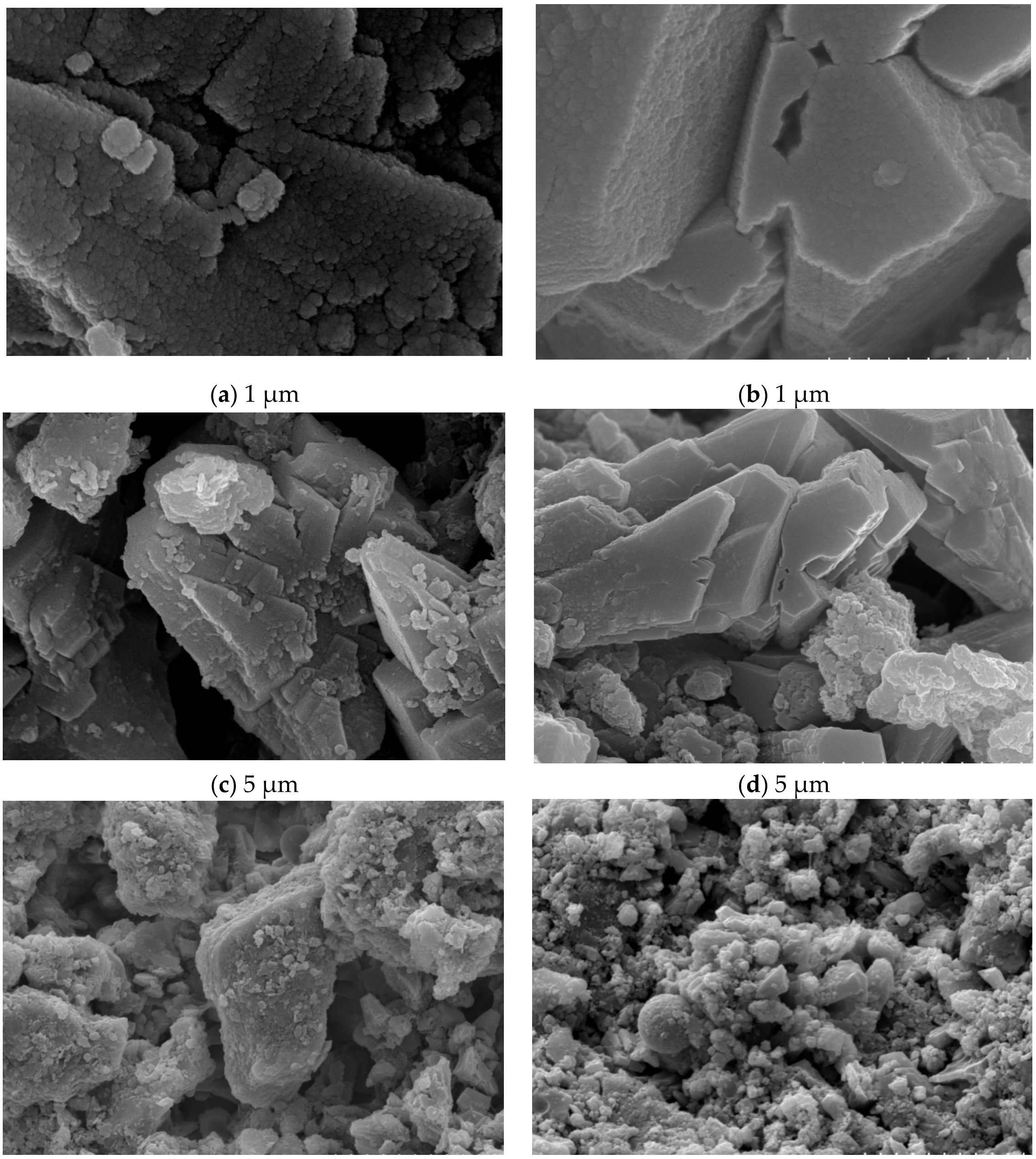
(e)

Figure 3. Changes of (**a**) Pb, (**b**) Cd, (**c**) Cu, (**d**) Zn, (**e**) Fe concentrations in effluent under different HRT.

From the above results, it can be seen that, with the extension of HRT, the hydraulic load decreases, the impact force of water flow decreases, and the contact time between wastewater and substrate extends, so the adsorption reaction takes place more thoroughly and more heavy metals in wastewater can be removed. At the same time, the contact time between plant roots and wastewater also increases simultaneously, which can strengthen the removal of heavy metals through metabolism and secretion of root substances. Therefore, with the extension of the operation time of the two groups of CWs devices, the HRT of the later device can be extended to 4 days without adjusting other parameters, so that the effluent concentration can meet the sewage discharge standard.

3.2. Microstructure and Adsorption Characteristics of Ceramsites in CWs

The surface morphology of ceramsite in two groups devices is shown in Figure 4. After the adsorption of heavy metals, the surface of UCWTR changed from columnar structure to agglomerated structure and accumulated into large particle structure. The surface of clay ceramsite changed from loose agglomerated structure to smooth and compact layered structure. The reason may be that there are many heavy metal elements in the wastewater, resulting in the formation of various heavy metal compounds on the surface of the ceramsites to fill the surface cracks. At the same time, the tested samples belong to the plant root layer of the CWs, and macromolecular substances such as organic acids secreted by the roots will react with the ceramsites and change its surface morphology.



(**a**) 1 µm (**b**) 1 µm

(**c**) 5 µm (**d**) 5 µm

(**e**) 20 µm (**f**) 20 µm

Figure 4. Surface image of CWs (**a**,**c**,**e**) UCWTR and (**b**,**d**,**f**) clay ceramsite.

The XPS analysis results of ceramsite in two groups of devices are shown in Figure 5. The characteristic peaks of O1s, Ca2p, C1s, Si2s and Al2p appear in the XPS broad spectrum of both ceramsites, indicating that both ceramsites contain O, Ca, C, Si and Al, which is consistent with the XRF analysis results in Table 1. After the adsorption of Pb and Cd, a new peak appears in the O1s spectrum of the two ceramsites, which may be formed by the combination of O on the ceramsite and Pb^{2+} or Cd^{2+} in the solution to form oxides. No characteristic peaks of heavy metals Pb, Cd, Cu, Zn were found in the full spectrum of UCWTR and clay ceramsite, indicating that the tested samples did not contain Pb, Cd, Cu, Zn or the content was lower than the detection limit of the instrument. This showed that the substrates in the two groups of CWs devices still have great adsorption potential for heavy metals in wastewater.

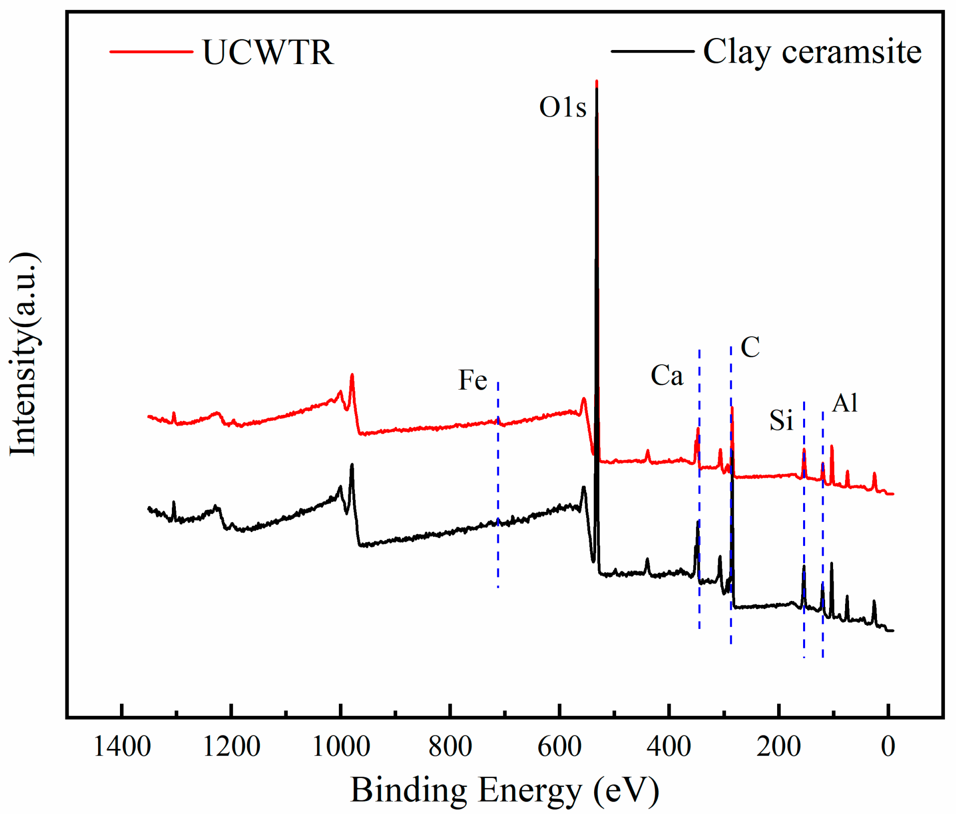


Figure 5. XPS spectra of CWs UCWTR and clay ceramsite.

The FT-IR analysis results of the ceramsite in two groups devices were shown in Figure 6. After running for 56 d, the characteristic peaks on the two kinds of ceramsites were basically the same, and there are characteristic peaks at wave numbers 3626 cm^{-1}, 3450.9 cm^{-1}, 1641.13 cm^{-1}, 1434.3 cm^{-1}, 1460.81 cm^{-1}, 1036.07 cm^{-1}, 1059.21 cm^{-1}, 788.74 cm^{-1}, 804.65 cm^{-1}, 531.29 cm^{-1}, 571.79 cm^{-1}, respectively [28], which originate from the stretching vibration peak of -OH, the vibration peak of C=O and O-Ca-O, the stretching vibration of Si-O-Si, the bending vibration of Al-OH and Si-Fe-O [29], which indicates that C-S-H gel formed by the combination of -OH, C=O, Al-OH and Si-Fe-O active groups and O-CA-O with -OH and Si-O-Si exists in both ceramides [30]. Compared with the clay ceramsite, the characteristic peak at 3627.45 cm^{-1} appeared on the UCWTR spectrum, and the movement of functional groups at 1651.73 cm^{-1} was enhanced, indicating that the ion exchange reaction, chelation reaction of -OH, and coordination reaction of C=O group of carboxyl group were enhanced. Therefore, the adsorption reaction of UCWTR for Pb, Cd, Cu, and Zn was enhanced, and the adsorption capacity was increased. Iron and aluminum oxides in UCWTR can react with Pb and Cd to form a stable reduced state, which increases the stability of heavy metals after reaction and reduces environmental risks [31]. Therefore, the adsorption mechanism of Pb and Cd on ceramsite is that they are first adsorbed on the surface of ceramsite through ion exchange, and then, under the action of -OH, C=O, Al-OH, Si-Fe-O, and C-S-H gel, coordination and chelation reactions take place to generate new substances. Compared with before adsorption, the -OH vibration of UCWTR was strengthened, and the C-H vibration was weakened, but the C-H on the clay ceramsite remained basically unchanged, which may be related to the increase of heavy metal ions in the wastewater. The enhanced adsorption reaction was also related to the enhanced iron-aluminum chelation reaction on UCWTR.

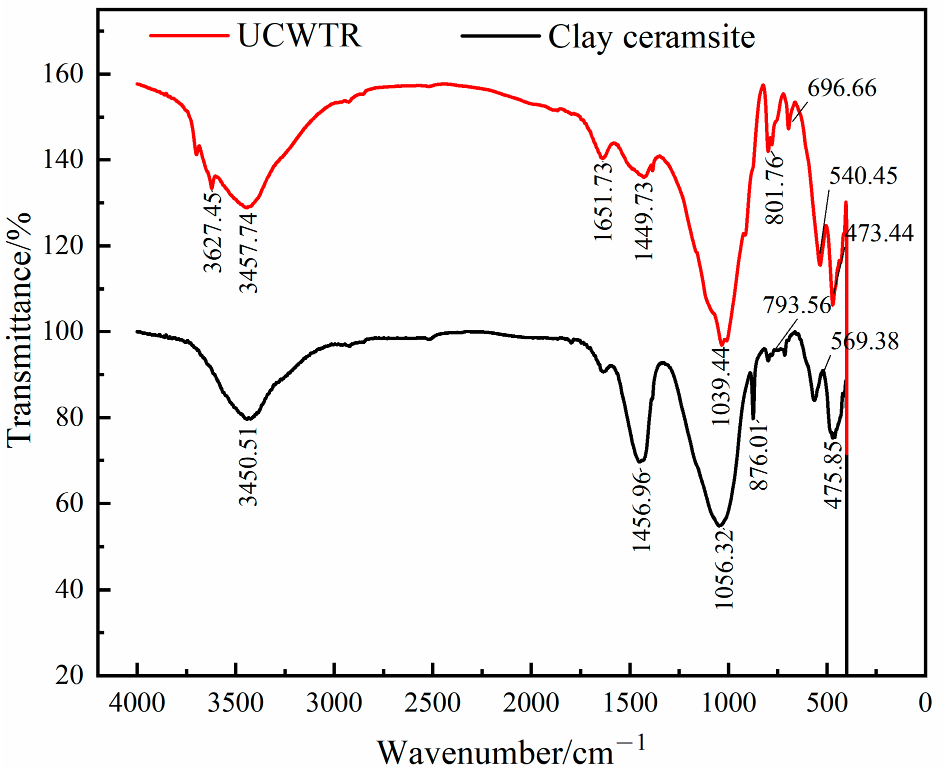


Figure 6. FT-IR of CWs UCWTR and clay ceramsite.

4. Discussions

Through the above experimental research, the following three conclusions can be drawn.

(1) After 56 days of operation, the two groups of devices mainly removed heavy metal ions in wastewater under the adsorption of the front-end substrate (0.2 m), and the latter-stage substrate and plants had less enrichment effects. With the increase of substrate distance in the horizontal direction, the concentration of heavy metals in wastewater continued to decrease. In the later period of operation (50 d), the substrate distance increased from 0.2 m to 0.8 m, and the concentrations of Pb, Cd, Cu, Zn, and Fe in the effluent of UCWTR-based CWs decreased by 92.44%, 98.44%, 86.57%, 91.46%, and 79.32%, respectively.

(2) The removal rates of Pb, Cd, Cu, Zn, and Fe in wastewater from UCWTR-based CWs all reached more than 98.5%, and the concentrations of Pb, Cd, Cu, Zn, and Fe in the effluent on the 56th day were 30.05%, 24.85%, 20.82%, 14.63%, and 7.91% lower than those of clay ceramsite CWs, respectively, which are obviously better than the treatment effect of clay ceramsite-based CWs. The concentrations of Pb, Cd, Cu, and Zn in the effluent water of UCWTR-based CWs all reached the "Integrated Wastewater Discharge Standard (GB 8978-1996)", but the concentration of Cd exceeded the Class V surface water quality standards after 38 days. This phenomenon indicates that UCWTR-based CWs have no obvious competitive adsorption advantage for Cd, and when UCWTR-based CWs is used to treat Cd up to 16.1 g, it is necessary to replace the filler in time to enhance the purification of Cd in wastewater.

(3) The concentrations of Pb, Cd, Cu, Zn, and Fe in the effluent of the two groups of devices were all inversely correlated with HRT, but the removal rates of heavy metals were all above 95% with the change of HRT. Without adjusting other parameters, the HRT of the later device can be extended to 4 days with the extension of operation time, which improves the purification efficiency of heavy metals.

5. Conclusions

The paper takes the UCWTR-based CWs as the research object, and proposes to use UCWTR as the substrate of the simulated CWs, in order to reduce the toxic effect of heavy metals in wastewater and make the complex wastewater of heavy metals such as mine wastewater meet the wastewater discharge standard. Through the simulated CWs test, the results showed that the two groups of devices mainly remove heavy metal ions in the wastewater under the adsorption of the front substrate (20 cm). With the increase of the horizontal substrate distance, the concentration of heavy metals in the wastewater continues to decrease. The removal rate of Pb, Cd, Cu, Zn, and Fe in wastewater by UCWTR-based CWs is more than 98.5%. On the 56th day, the concentration of Pb, Cd, Cu, Zn, and Fe in effluent is 30.05%, 24.85%, 20.82%, 14.63%, and 7.91% lower than that of clay ceramsite-based CWs, respectively, which is obviously better than that of clay ceramsite based CWs. This result provides a scientific basis for simultaneously solving the resource utilization of residual sludge in water supply plants and realizing the efficient treatment of mine wastewater. Later, the research team will further carry out relevant research on the possible secondary pollution and the recycling of ceramsite after the adsorption of ceramsite.

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Abbreviations

WTR	Water treatment residuals
UCWTR	Unburned ceramsite water treatment residuals
CWs	Constructed wetlands
AMD	Acid mine drainage
DO	Dissolved oxygen
HRT	Hydraulic retention time
COD	Chemical oxygen demand
NH_4-N	Ammonia nitrogen
TN	Total nitrogen
TP	Total phosphorus

Nomenclature

Name	Unit of measurement
Concentration	mg/L
Distance	m
Adsorption capacity	mg/g
Time	d
Flow	L/min

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